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EXHAUSTIVE FRACTIONATION OF THE "EXTRACT" PORTION OF THE LUBRICANT FRACTION FROM A MID-CONTINENT PETROLEUM[1]*

By Beveridge J. Mair[2] and Charles B. Willingham[2]

ABSTRACT

This paper describes the separation, by distillation and extraction, of the extract portion of the lubricant fraction from a midcontinent petroleum. After a preliminary separation of the "asphaltic" material, the remainder of the sulfur dioxide-soluble material and the silica gel "hold-up" were combined and systematically distilled until substantially constant-boiling fractions were obtained. Five charges of these fractions with narrow-boiling ranges were then prepared and each charge of from 500 to 700 g was separated into 30 to 40 fractions by reflux extraction with methyl cyanide, or methyl cyanide containing acetone, in 16.7-m columns. Kinematic viscosities at 100° and 210° F, refractive indices, densities, refractive dispersions, specific optical rotations, and aniline points were determined for most of the fractions from the extraction process. In addition, for 41 "key" fractions there are reported boiling points, molecular weights, and carbon-hydrogen ratios, and for some of these fractions there are given the percentages of sulfur, nitrogen, and oxygen. Attention is called to a number of interesting facts in connection with the properties of these petroleum fractions.

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[1] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of Project 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

[2] Research Associates at the National Bureau of Standards, representing the American Petroleum Institute.

*This paper was originally presented before the Petroleum Division of the American Chemical Society at Milwaukee on September 8, 1938.

I. INTRODUCTION

Two years ago this laboratory reported the results of an investigation [1, 2][3] of the chemical composition of a "water-white" oil prepared from the lubricant fraction of a midcontinent petroleum. To obtain a more complete picture of the whole lubricant fraction of petroleum, a similar investigation has been made on portions of the same fraction which were soluble in sulfur dioxide and retained by silica gel. After a preliminary separation of the asphaltic material, the remainder of the sulfur dioxide extract and the material retained by silica gel were combined and then separated, first by repeated distillations in high vacuum and then by extraction with methyl cyanide.

A correlation of the physical properties of certain fractions from this extraction process, and their comparison with those obtained in the investigation of the water-white oil and with synthetic hydrocarbons, follow in a subsequent paper.

II. ORIGIN OF THE MATERIAL AND OUTLINE OF THE INVESTIGATION

The lubricating-oil stock came from well No. 6 of the South Ponca Field, Kay County, Okla. Before delivery to the Bureau, the oil was distilled in vacuo by the Sun Oil Co., Philadelphia, Pa. Treatment of the oil at this Bureau has been described elsewhere [1, 2, 3] and is illustrated diagrammatically in figure 1. It consisted in (1) The separation of an extract portion by extraction with liquid sulfur dioxide at room temperature, (2) the separation of a "wax" portion by crystallization from ethylene chloride at −18° C, and (3) the separation of the remainder into two portions by filtration through silica gel: (a) a water-white portion, whose investigation has already been reported [1, 2], and (b) a portion recovered from silica gel and listed in figure 1 as silica gel hold-up.

This paper deals only with the investigation of the sulfur dioxide-soluble portion and the silica gel hold-up. As shown in figure 1, the present fractionation was begun by separating the extract portion into two parts by extraction with sulfur dioxide and petroleum ether at −55° C. The portion soluble in sulfur dioxide at −55° C, denoted in figure 1 as asphaltic material, was placed in storage. The petroleum ether-soluble portion was combined with the material recovered from silica gel and the mixture submitted to a systematic fractional distillation in high vacuo. After the distillation had progressed as far as was profitable, fractions, represented in figure 1 as distillation keys, were selected and a number of their physical properties determined. Five charges, designated as *A*, *B*, *C*, *D*, and *E*, of from 500 to 700 g each, were then prepared for extraction by mixing according to their viscosities the individual distillation fractions of about 70 g each. These charges amounted to a little less than one-third of the total weight of the distillate and represented the greater part of the distillation range. Each charge was separated into 30 to 40 fractions of about 15 g each by extraction with methyl cyanide, or with methyl cyanide containing some acetone for the less soluble fractions. Kinematic viscosities at 100° and 210° F, and refractive indices at 25° C, were determined on all the fractions from the extractors. Densities,

[3] Figures in brackets indicate the literature references at the end of this paper.

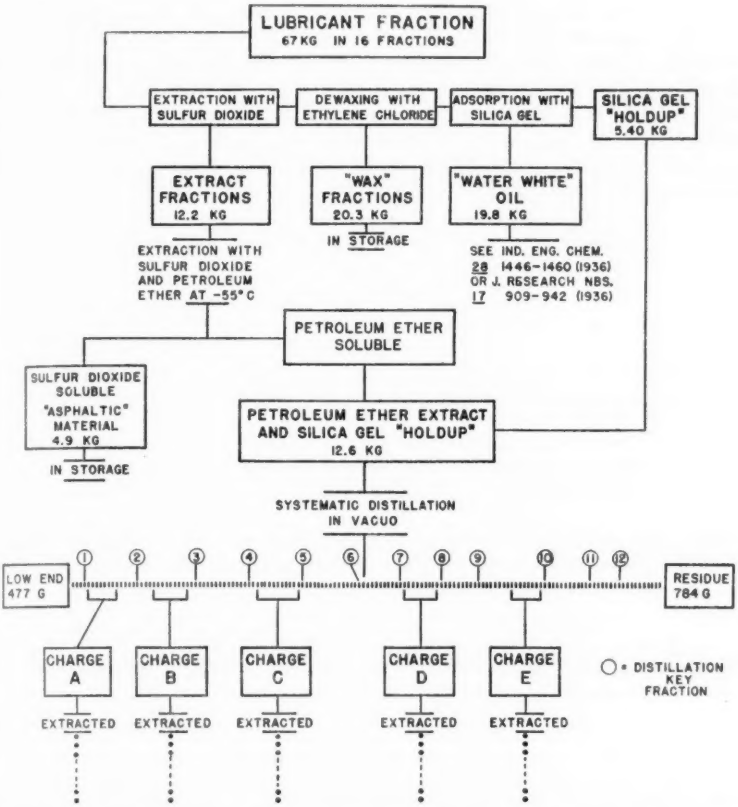
LUBRICANT FRACTION
67 KG IN 16 FRACTIONS
EXTRACTION WITH SULFUR DIOXIDE
DEWAXING WITH ETHYLENE CHLORIDE
ADSORPTION WITH SILICA GEL
SILICA GEL "HOLDUP" 5.40 KG
EXTRACT FRACTIONS 12.2 KG
"WAX" FRACTIONS 20.3 KG
"WATER WHITE" OIL 19.8 KG
IN STORAGE
EXTRACTION WITH SULFUR DIOXIDE AND PETROLEUM ETHER AT −55° C
SEE IND. ENG. CHEM. 28 1446–1460 (1936) OR J. RESEARCH NBS. 17 909–942 (1936)
PETROLEUM ETHER SOLUBLE
SULFUR DIOXIDE SOLUBLE "ASPHALTIC" MATERIAL 4.9 KG
IN STORAGE
PETROLEUM ETHER EXTRACT AND SILICA GEL "HOLDUP" 12.6 KG
SYSTEMATIC DISTILLATION IN VACUO
LOW END 477 G
RESIDUE 784 G
CHARGE A
CHARGE B
CHARGE C
CHARGE D
CHARGE E
EXTRACTED
DISTILLATION KEY FRACTION

FIGURE 1.—*Chart showing treatment and disposition of lubricating-oil fractions.*

refractive dispersions, aniline points, and optical rotations were determined on most of them. In addition, carbon-hydrogen ratios, molecular weights, and boiling points were determined on 41 key fractions, and on some of these the percentages of sulfur and nitrogen were also determined.

III. PRELIMINARY TREATMENT BEFORE DISTILLATION

1. SULFUR DIOXIDE-SOLUBLE PORTION

It seemed probable that the extremely viscous, semisolid material contained in the sulfur dioxide-soluble portion would be difficult to "degas", would probably froth and bump in the stills, and make difficult, if not impossible, the operation of the extractors. To avoid these difficulties a preliminary separation was made:

In a 3-liter Pyrex flask about 500 to 600 g of oil was obtained in solution (or suspension) in 1,600 ml of petroleum ether (bp 30° to 60° C), by vigorous stirring at room temperature. The temperature was lowered to about −15° C, at which point 500 ml of liquid sulfur dioxide was added, and, while still stirring vigorously, the tempera-

ture was lowered to −50° to −60° C. The petroleum ether layer was siphoned off, and the sulfur dioxide layer reextracted with four 1,500-ml portions of petroleum ether. Data on cut 23, which was extracted three times, are given in table 1. It was evident that the amount removed by successive extractions with petroleum ether became rapidly less, and after a fifth extraction it was concluded that little material would be separated by further extraction with petroleum ether in this way.

TABLE 1.—*Weights and refractive indices illustrating the separation of cut 23*[a]

Fraction	Weight	Refractive index n_D^{25}
	g	
SO_2-soluble	279	Too dark to measure.
First petroleum ether layer	308	1.578.
Second and third petroleum ether layers	108	1.586.

[a] Cut numbers here and throughout this paper refer to the original identification marks on the fractions as received from the Sun Oil Co. These numbers go from 23 for the lowest-boiling material to 38 for the highest. See table 2 in reference [3].

Some physical properties of the material soluble in sulfur dioxide at −55° C are recorded for two fractions in table 2, while table 3 records certain physical properties of the petroleum ether-soluble material.

TABLE 2.—*Physical properties of material soluble in sulfur dioxide at −55° C*

Fraction	Cut 23	Cuts 37 and 38
Softening point [a] (ring-and-ball method) (° C)	Too soft	49.6
Insoluble in petroleum ether [a] at room temperature (percent)	8.5	37.8
Refractive index $\left(n_D^{25}\right)$ of the portion soluble in petroleum ether	1.66	1.67

[a] The data on softening point and insoluble in petroleum ether recorded in this table were obtained by O. G. Strieter, Research Associate at the National Bureau of Standards, representing the Asphalt Shingle and Roofing Institute.
[b] This petroleum ether distilled from 35° to 60° C.

TABLE 3.—*Physical properties of the portion soluble in petroleum ether*

Fraction	Kinematic viscosity at		Kinematic-viscosity index	Refractive index n_D^{25}
	100° F	210° F		
	Stokes	*Stokes*		
Cut 24	1.37	0.0736	−148	1.573
Cut 30	4.09	.121	−192	1.575
Cut 35+36	49.1	.445	−184	1.508

2. MATERIAL RECOVERED FROM SILICA GEL

The silica gel hold-up was extremely dark in color, so, with a small portion, an attempt was made to remove black asphaltic material by treatment with sulfur dioxide and petroleum ether at −55° C. However, since practically the entire fraction was found to be soluble in the petroleum ether layer, this treatment was not continued.

Certain physical properties of the silica gel hold-up are given in table 4. It was not possible to get refractive indices with any high degree of precision, owing to the highly colored nature of this material.

TABLE 4.—*Physical properties of silica gel hold-up*

Fraction	Kinematic viscosity at—		Kinematic-viscosity index	Refractive index n_D^{25}
	100° F	210° F		
	Stokes	*Stokes*		
Cut 23 to 28	2.93	0.127	−52	1.54 to 1.55
Cut 29 to 32	6.81	.182	−95	1.54 to 1.55
Cut 33 to 38	8.85	.261	−3	1.52 to 1.53

3. COMBINATION OF THE MATERIAL SOLUBLE IN PETROLEUM ETHER WITH THAT RECOVERED FROM SILICA GEL

The silica gel hold-up and the petroleum ether-soluble portion of the extract were now combined into three charges for distillation and some physical properties of these charges determined. These properties are given in table 5.

TABLE 5.—*Properties of the petroleum ether-soluble portion combined with the portion retained by silica gel*

Fraction	Kinematic viscosity at—		Kinematic-viscosity index	Refractive index n_D^{25}	Sulfur content	Nitrogen content
	100° F	210° F				
	Stokes	*Stokes*			*Percent by wt*	*Percent by wt*
Cut 23 to 28	2.97	0.113	−123	1.562	0.94	0.14
Cut 29 to 32	7.23	.171	−153	1.568	.98	.10
Cut 33 to 38	18.84	.322	−82	1.557	.87	.14

IV. DISTILLATION EQUIPMENT AND PROCEDURE

The oil was systematically distilled in a battery of six simple molecular stills of the type used in the distillation of the water-white oil [3]. These stills were 12 cm in diameter and were charged with 420 to 500 g of oil. Each charge yielded six distillate fractions and one residue, each of 60 to 70 g. The receivers, one of which is shown schematically in figure 2, were of the type previously described, but modified to permit the removal of fractions with a siphon. Referring to figure 2, oil from the still flowed through tube *B* to funnel *C*, and then to one of the six (only two are shown) receivers, *D*. The funnel contained a soft-iron core and was directed to the individual receivers by the action of an Alnico magnet on this core. The fractions were transferred to the sample bottles by means of a siphon, inserted through the ground joint *A* and extending to the well in the bottom of each receiver. This procedure has two advantages: The oil does not at any time come into contact with the ground joints; leakage is minimized by the reduction in number, from six to one, of ground joints for each receiver.

There was a drainage problem with this very viscous oil, and consequently tube *B* through which the distillate passed to the receiver, was electrically heated nearly to the temperature of distillation. Also to cause the oil to drain as completely as possible, the receivers were surrounded with beakers of water kept at 90° C, and at least an hour was allowed between the time of removal of the bulk of the sample and the removal of the drainage. Auxiliary equipment was used to heat the siphons to avoid drainage losses. Precautions were also taken to avoid large losses in transferring the oil from the sample bottle to the stills. The sample bottles were heated in a special container on the steam bath so that the entire bottle up to the neck was hot, and as much oil as possible was transferred to the still. The oil still retained in the bottles, constituting a single charge, was washed out with ether, the ether removed, and the oil transferred to the still by means of a small flask.

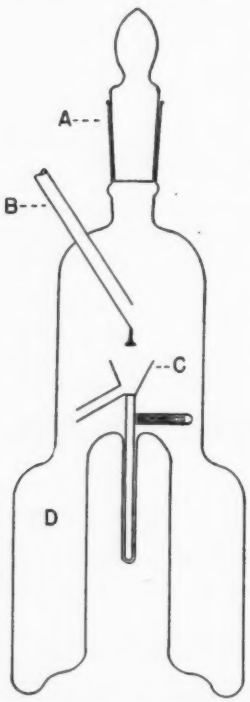

FIGURE 2. *Receiver for vacuum distillation.*

During the first distillation considerable difficulty was experienced with frothing and sputtering, which may have been due to small traces of petroleum ether which had not been completely removed. After this distillation little difficulty was experienced except with a few of the most viscous charges. The procedure adopted to avoid frothing was to reduce the viscosity of the oil by warming it to about 40° to 60° C below its distillation temperature, and then to reduce the pressure slowly.

A period of about 7 hours was required for charging the stills and degassing the charges, and an equal period for the distillation of the six fractions. The noncondensible gas pressure as read on a McLeod gage was usually about 10^{-4} mm Hg. The temperature of distillation varied from 95° C for the lowest-boiling fractions to about 210° C for the highest-boiling fractions. The highest temperature of distillation of any fraction subsequently extracted was about 170° C. After a distillation had been completed, carbon dioxide was admitted to the system, and the fractions were stored in an atmosphere of carbon dioxide until the next distillation. The color of the distillation fractions varied as the boiling point increased from yellow to deep orange red. The black material originally present remained in the residues from the distillation.

As with the water-white oil, the viscosity of the distillation fractions increased continuously with increase in boiling point, and consequently viscosity was used as the basis for mixing fractions for successive distillations. The viscosity at 210° F was used primarily for this purpose, since less material was retained by the pipettes at this higher temperature.

On the right of figure 3 are shown the ranges of viscosities of the fractions which were mixed to prepare some of the charges for the eighth distillation, while in the main part of the figure the viscosities of the fractions resulting from this distillation are plotted with respect to the percentage of the charge distilled. The range in viscosity of the fractions resulting from the distillation of any one charge was not much greater than the range in viscosity of the fractions mixed to prepare the charge, and it was therefore considered unprofitable to continue further the distillation.

Although the range in viscosity of the fractions from the more viscous charges is much greater than that for the fractions from the

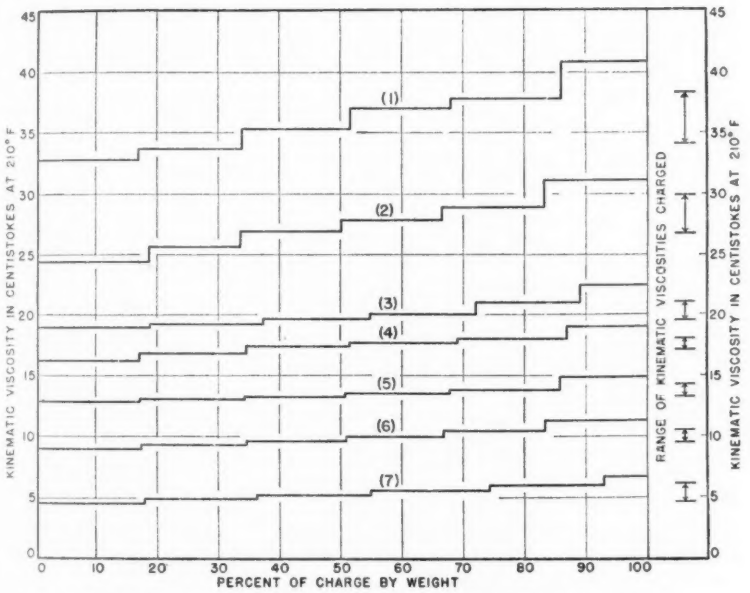

FIGURE 3. *Viscosities of fractions from the final distillation.*

less viscous charges, the ranges in boiling point of the two series of fractions do not differ greatly. Thus, the ranges in boiling point of the fractions given in curves (2) and (6) of figure 3 (computed from figure 4) are about the same, namely, 10° C.

After the eighth distillation, there were 144 fractions (see fig. 1) with a total weight of 9,970 g, an undistilled residue of 784 g, and a more volatile portion of 477 g, removed at earlier stages from the systematic distillation.

V. PROPERTIES OF DISTILLATION FRACTIONS

Before proceeding to the extraction process, certain properties were determined on 12 selected distillation fractions, covering practically the entire boiling range. These distillation key fractions are indicated in figure 1, and their properties are listed in table 6.

TABLE 6.—*Physical properties of distillation key fractions*

Key fraction (see fig. 1)	Kinematic viscosity at		Kinematic-viscosity index	Refractive index n_D^{25}	Density at		Density extrapolated 77° F= 25° C	Refractive dispersion $n_F - n_C$ at 25° C	Specific optical rotation at 100° F $[\alpha]_D$	Boiling points at 1 mm Hg	Molecular weight	Combustion analyses		Percentage (by weight) of			In the formula C_nH_{2n+z}		Aniline points
	100° F	210° F			100° F	210° F						Ratio: moles H_2O/CO_2	Mass of sample less mass of C+H	S	N	O by diff.	n	z	
	Stokes	*Stokes*			*g/ml*	*g/ml*	*g/ml*			°C			*Percent by wt of sample*						°C
1	0.687	0.0559	−88	1.5590	0.9705	0.9299	0.9794	0.0195	+0.19	176.6	287	0.6861	1.26	0.76	0.03	0.47	21.1	−13.3	7.2
2	1.76	.0849	−136	1.5634	.9780	.9362	.9869	.0199	.41	196.6									12.7
3	2.84	.105	−159	1.5648	.9803	.9392	.9892	.0202	.55	204.6	330	.6861	1.44	.93	.04	.47	24.3	−15.2	16.8
4	4.09	.126	−161	1.5630	.9794	.9374	.9883	.0200	.63	214.0									20.3
5	5.68	.145	−181	1.5650	.9815	.9398	.9904	.0200	.69	218.8	351	.6931	1.42	.94	.07	.41	25.8	−15.8	21.5
6	6.80	.167	−148	1.5629	.9810	.9367	.9899	.0199	.58	225.6									23.5
7	(8.90)	.189	−158	1.5629	.9823	.9381	.9912	.0197	.57	232.2	372	.7045	1.49	.88	.09	.52	27.3	−16.1	28.3
8	10.8	.213	−147	1.5622	.9770	.9371	.9859	.0199	.62	238.1									30.3
9	14.3	.244	−154	1.5625	.9799	.9374	.9888	.0197		244.1									32.6
10	28.9	.353	−153	1.5630	.9803	.9364	.9892	.0197		260.6	429	.7132	1.62	.94	.14	.54	31.4	−18.0	37.8
11	38.9	.442	−116	1.5592	.9774	.9338	.9863	.0193		275.7									45.9
12	50.0	.540	−85	1.5570	.9728	.9308	.9817	.0189		289.2	491	.7387	1.56	.83	.18	.55	35.9	−18.7	52.6

The methods and apparatus for determining these properties are discussed in section VIII, p. 548.

It may be noted that the molecular weight, viscosities, and aniline points increase with increasing boiling point. The refractive indices, densities, and refractive dispersions of the first and last fractions are somewhat lower than those of the rest, while the viscosity indices are higher. This variation is, however, negligible when compared with the large variations produced by the subsequent extraction process, and indicates that substantially no type separation was effected by distillation. The optical rotation increases up to about the third key

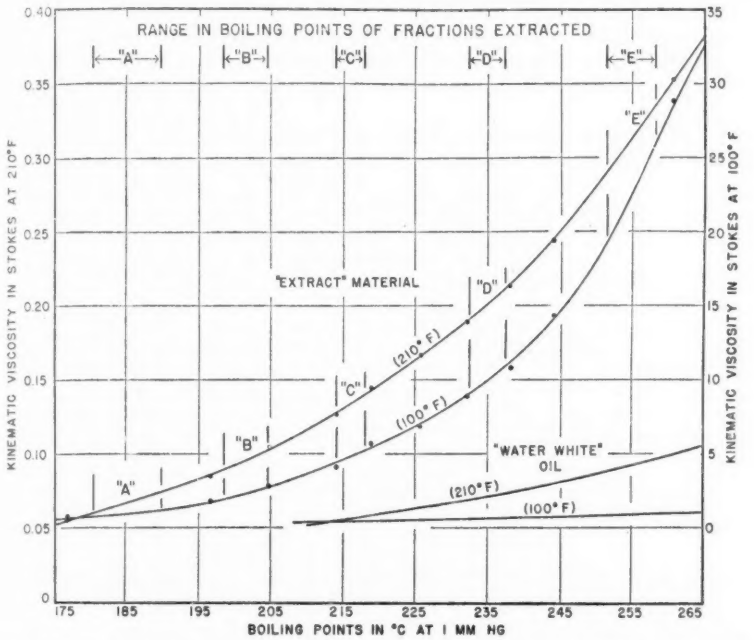

FIGURE 4.—*Relations between viscosity and boiling point for distillation fractions of the extract material and of the water-white oil.*

The boiling-point ranges of the fractions mixed to prepare the changes for extraction are also shown.

fraction and from there on remains substantially constant to the eighth key fraction.

It is to be noted that these fractions contain from 1.2 to 1.6 percent by weight of elements other than hydrogen and carbon. The sulfur and oxygen contents do not vary greatly throughout these fractions, but the nitrogen content increases from 0.03 to 0.18 percent with increase in molecular weight. Although the percentage of hydrogen increases from 10.1 to 10.8 from the first to the twelfth fraction, the deficiency of hydrogen as given by the x value in the formula C_nH_{2n+x} increases from -13.3 for the first to -18.7 for the twelfth fraction.

Some of the relationships between physical properties are shown graphically in figures 4 and 5. In figure 4 are also shown the relationships between boiling point and viscosities at 100° and at 210° F for distillation fractions of the water-white oil [3]. It has been observed

by other investigators that the viscosities of extract fractions for given boiling points are much higher than those of raffinate fractions, and a comparison of the viscosities of these extract fractions and water-white oil fractions once more emphasizes this point. There is also shown in figure 4 the range in boiling points and viscosities of the fractions subsequently mixed to prepare for the extractors charges *A*, *B*, *C*, *D*, and *E*.

In figure 5 are plotted on a logarithmic scale the viscosities at 210° F with respect to those at 100° F for a number of the distillation fractions. The points fall on a line with only a slight curvature. Indeed, a straight line represents the data fairly well between 2 and 25 stokes

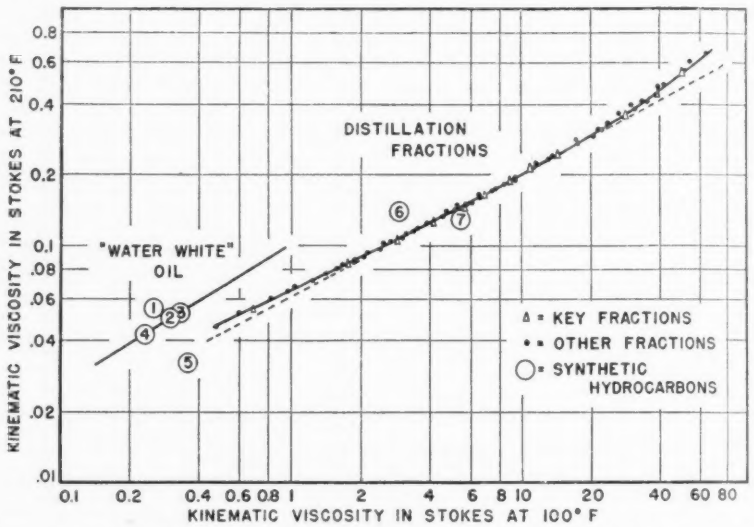

FIGURE 5.—*Logarithmic scale of the viscosity at 210° F against that at 100° F for distillation fractions of the extract material and of the water-white oil.*

The numbers represent values for synthetic hydrocarbons as follows:
(1) 16-*n*-Butylhentriacontane.
(2) 1-Cyclohexyl-2-hexahydrobenzylheptadecane.
(3) 1,1-Dicyclohexylhexadecane.
(4) 1,1-Diphenylhexadecane.
(5) Dihydrodiethylanthracene.
(6) Dihydrodi-B-octylanthracene.
(7) Dihydrodiisoamylanthracene.

at 100° F. Below and above these viscosities the deviation from the linear becomes more pronounced. These deviations correspond with the lower refractive indices, lower dispersions, and higher viscosity indices found for these fractions, and indicate a slight change in the type of material. Also shown in this figure for comparison is a plot of the viscosities of the water-white oil distillation fractions and several synthetic hydrocarbons.[4] A plot of this nature is useful in checking errors in the determination of viscosity. In cases where large deviations from these curves were found redetermination invariably brought the points closer to the curve.

[4] The values for the synthetic hydrocarbons were obtained by interpolation or extrapolation with the aid of Cragoe's equation [4] from the original data, which extended from approximately 20° to nearly 100° C, of Suida and Planckh [5] for 16-*n*-butylhentriacontane; Landa and Cech [6] for 1,1-dicyclohexylhexadecane, 1-cyclohexyl-2-hexahydrobenzylheptodecane, 1,1-diphenylhexadecane; and Lerer [7] for dihydrodiethylanthracene, dihydrodi-*β*-octylanthracene, and dihydrodiisoamylanthracene.

VI. PRELIMINARY EXPERIMENTS WITH SOLVENTS

Acetone, the solvent used in the extraction of the water-white oil, could not be used with the oil under investigation, because of the high solubility of the oil in it. Consequently, a few preliminary experiments were made to determine the solubility of the material under investigation in a number of solvents and to obtain an approximate measure of the selectivity of the solvents. These experiments were confined to low-boiling solvents which could be readily removed from the oil.

Two fractions were used in this work: One, having a kinematic viscosity of 0.0244 stoke at 210° F, came from the low-boiling end of the distillation range and had a boiling point below 175° C at 1 mm Hg; the other, having a viscosity of 0.275 stoke at 210° F, came from well up in the distillation range and had a boiling point of 249° C at 1 mm Hg.

The results of the solubility and selectivity tests shown in table 7 were obtained by shaking the oil and solvent in a separatory funnel, separating the phases, and removing the solvent. After reading the refractive indices, the dissolved and undissolved portions were recombined and the same oil was used with the next solvent.

TABLE 7.—*Results of preliminary experiments with several solvents*

Fraction	Weight	Refractive index n_D^{25}	Solvent	Volume of solvent	Temperature
	g			*ml*	*°C*
Original oil (KV_{210}=0.0244)	75	1.5368			
Undissolved	12	1.5098	Methyl formate	450	+15
Dissolved	63	1.5436			
Undissolved	43	1.5199	Methyl cyanide	450	+30
Dissolved	31	1.5637			
Undissolved	30	1.5247	Acetone+Water [a]	155	0
Dissolved	43	1.5474			
Undissolved	44	1.5284	Methyl alcohol	450	+25
Dissolved	24	1.5518			
Undissolved	34	1.5120	Sulfur dioxide	150	−25
Dissolved	34	1.5620			
Original oil (KV_{210}=0.2753)	54	1.5630			
Undissolved	47	1.5579	Methyl cyanide	450	+30
Dissolved	7	1.6117			
Undissolved	29	1.5498	Acetone,[b] + Water	200 / 5	+25
Dissolved	25	1.5789			

[a] Completely miscible in pure acetone to −25° C. This 155 ml of solvent was composed of 150 ml of acetone plus 5 ml of water.
[b] Completely miscible in pure acetone at room temperature.

It is evident from the data in table 7 that the lower-boiling fraction is too soluble in either sulfur dioxide or acetone to permit the use of these solvents at room temperature. The use of solvents at much below room temperature in the type of columns used (see p. 546) is considered impractical, owing to the extremely high viscosity of this oil at low temperatures. Methyl formate also dissolves too much of the lower-boiling fraction, and is excluded, moreover, because its density (D_{20}=0.975) is between that of the fractions (D_{25}=0.85−1.08) obtained in the systematic extraction. From the point of view of solubility (at least for the lower-boiling fractions), both methyl alcohol and methyl cyanide appear satisfactory.

To determine the relative selectivity of solvents, some physical property which changes markedly with type of molecule should be compared for equal percentages extracted. While such data have not been obtained, it is possible to get some idea as to the selectivity from the spread in refractive indices given in table 7. It is evident that methyl cyanide is more selective than methyl alcohol, and at least as selective as any of the other solvents tested, with the exception of sulfur dioxide.

Preliminary experiments indicated that a short extractor operated satisfactorily with the lower-boiling fractions when used with pure methyl cyanide. However, with the higher-boiling fractions, a mixture containing 20 to 30 percent of acetone was required to obtain satisfactory operation.

VII. EXTRACTION EQUIPMENT AND PROCEDURE

The extractor columns used in this investigation were essentially the same as those used in the extraction of the water-white oil with acetone [1]. This type of column has been described by Cannon and Fenske [8]. The columns were increased in height to 16.7 m. When filled with water, most of the flasks at the bottom of the extractors broke. The old flasks were replaced with heavy-walled Erlenmeyer flasks (500 ml) set in plaster of paris and mounted on an iron frame. Additional capacity was obtained by sealing tubes 4 cm in diameter and 10 cm long to the neck of the Erlenmeyer flask rather than by using Erlenmeyer flasks with larger bases. Also, the bottoms of the Erlenmeyer flasks were blown slightly convex. With these changes the vessels withstood the hydrostatic pressure, and no breakage occurred throughout the work.

It had also been found in preliminary work with a short extractor column that considerable color was produced in the fractions. This production of color was undoubtedly due to oxidation, since it was very materially reduced by maintaining an atmosphere of carbon dioxide over the boiling methyl cyanide. Throughout the systematic extraction a stream of carbon dioxide, under a head of 10 mm of oil, was passed through the top of the condenser.

The operation of the extractor columns was essentially the same as with the water-white oil and acetone. The extraction of charges *A*, *B*, and *C* was begun with pure methyl cyanide (constant-boiling from a 30-plate column). For charges *D* and *E*, because of the somewhat lower solubility of this material, a mixture of 75 percent of methyl cyanide plus 25 percent of acetone was used at the beginning. In the extraction of charges *A*, *B*, and *C* the reflux of oil globules was quite as satisfactory as was obtained with the water-white oil and acetone. However, for a number of the fractions at the beginning of the extraction of *D* and *E*, only a small part of the reflux returned as globules, since the greater part formed a stream which flowed down the walls of the column. This condition is undoubtedly associated with the extremely high viscosity of the first few fractions from these extractors (*E–9* has a viscosity of 886 stokes at 100° F.) It was not until about the fifth fraction for extractor *D*, and the twelfth fraction for extractor *E*, that these columns began to function normally.

Throughout the greater part of the extraction of a charge, it is possible to control the size of the fractions simply by varying the amount

of methyl cyanide in the boiler (100 to 400 ml). There is, however, a certain point where the solubility becomes so low that even with the boiler full (400 ml) the size of the oil fractions is too small, and it becomes advisable to change or modify the solvent. It should also be pointed out that when the solubility becomes too low (that is, below about 0.8 to 1 g per 100 ml of methyl cyanide) the column does not operate satisfactorily. Consequently, after removal of fraction *"A–29"*, 300 ml of acetone instead of methyl cyanide was charged into the column and the extraction completed by adding acetone instead of methyl cyanide. For extractor *B*, 350 ml of acetone was charged at fraction 32, and from this fraction to the end of that series an attempt was made to regulate the size of the oil fractions by charging, as seemed desirable from the weight of the preceding fraction, either methyl cyanide or acetone or a mixture. The same procedure was adopted for extractor C at fraction 29.

For extractors *D* and *E*, as mentioned previously, a mixture of 75 percent of methyl cyanide with 25 percent of acetone by volume was used at the beginning. At *D–24* and *E–20*, the size of the fractions was controlled by increasing the percentage of acetone. Even with this procedure, the decrease in solubility for the last few fractions from all of the extractors was usually so pronounced that it was necessary in some cases to combine adjacent fractions to obtain a portion as large as was required. In operating a column of this type with a mixture, it can be seen that when equilibrium is reached the concentration of acetone in methyl cyanide will be constant throughout the column except for the boiler, where a higher percentage of the higher-boiling component (methyl cyanide) will exist. Hence, since the oil-solvent fractions removed from the boiler were richer in methyl cyanide, the concentration of acetone in columns *D* and *E* undoubtedly increased above the average of 25 percent by volume.

After reflux commences, the less soluble portion returns to the oil reservoir and the more soluble oil takes its place; consequently, there is an increase in the density of solution in the reflux leg of the extractor. To balance this increase in density, an increase in the hydrostatic head in the solvent leg is necessary. When equilibrium is reached there should be no further increase in density in the reflux leg, and the liquid level in the solvent leg should reach (if no other factors were to be considered) a constant maximum. For extractor *A* this maximum occurred about 16 hours after reflux commenced, and the height was fairly constant. Other factors, however, influence this height, such as rate of circulation of solvent and viscosity of the oil in the reservoir, and, since a few degrees drop in temperature cause a pronounced increase in viscosity, this height was not very constant for the other extractors, and the time, though longer than for extractor *A*, could not be accurately determined. To be on the safe side, 24 hours was allowed for equilibrium for extractors *A* and *B*, 36 hours for *C* up to fraction 7 and from this point on, 24 hours, 48 hours for *D* and *E* up to fractions 5 and 7, respectively, when they were put on a 36-hour schedule to fractions 18 and 17 and from there on, 24 hours.

The solvent was removed from the fractions by maintaining them at 100° to 110° C in a stream of carbon dioxide for 2 to 3 hours. The pressure was then reduced to 27 mm, and sweeping out with carbon dioxide at the same temperature was continued for an additional 2 to 3 hours.

The fractions were stored in an atmosphere of carbon dioxide in small glass bottles fitted with rubber stoppers which had been boiled with a solution of sodium hydroxide to remove free sulfur. After about 2 months there were again signs of sulfur appearing on some of the stoppers, so they were replaced with Neoprene stoppers. There was no evidence of contamination of the samples by the stoppers.

VIII. DETERMINATION OF PROPERTIES

In general, the same methods of determining the physical constants were used as with the water-white oil [1, 2]. However, complications were introduced in many cases by the extreme viscosity of some of the fractions, their high temperature coefficients of viscosity, their color, and by the fact that they contained sulfur and nitrogen.

1. VISCOSITY [5]

Kinematic viscosities were determined at 100° and 210° F with the aid of the assembly of viscosity pipettes previously described. The pipettes were furnished with removable sintered-glass filter tips and were filled by drawing the oil through these tips. Duplicate determinations were made, and the precision of the recorded results is considered to be about ±1 percent for the fractions with high temperature coefficients of viscosity and about ±0.2 percent for fractions with small coefficients. The temperatures of the baths were usually constant to within ±0.03° F. The equipment available was not satisfactory for determining the viscosity at 100° F of a few of the most viscous fractions from charges *C*, *D*, and *E;* consequently, their viscosities were not determined. Kinematic-viscosity indices were computed with the aid of the tables given by Hersh, Fisher, and Fenske [9].

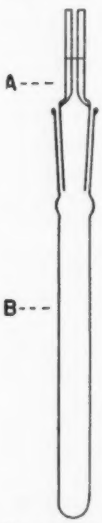

FIGURE 6.—*Picnometer for viscous oils.*

2. DENSITY [6]

Densities of the distillation key fractions were determined at 100° and 210° F with the aid of the same series of viscosity pipettes, each value recorded being the result of two determinations agreeing within ±0.0003 g/ml. For the extraction fractions, owing to the very viscous nature of some of them, it was preferable to use a picnometer of about 8-ml capacity of the type shown in figure 6. After being filled, the picnometer was immersed to 8 mm from the calibration mark, and the upper end of the capillary tube, *A*, was warmed gently with a flame to reduce the viscosity and hasten drainage. With an eye dropper inserted in tube *A*, the oil level was adjusted to the calibration mark. Duplicate determinations were made, and a precision of ±0.0003 g/ml was obtained.

Densities of five samples, *C–1*, *D–1*, *E–1*, *E–8*, and *E–13*, which were thought to be too viscous to observe in the picnometer, were determined by weighing in water by the Bureau's Capacity and Density Section. The results for these fractions are believed to be accurate to ±0.002 g/ml.

[5] The authors are indebted to P. Schoonover, C. L. Miller, and F. W. Melpolder, who made the viscosity determinations, and to F. W. Rose, Jr., who supervised these determinations.

[6] The authors are indebted to A. J. Streiff for his assistance in determining densities of these samples.

3. REFRACTIVE INDEX AND REFRACTIVE DISPERSION

Refractive indices were obtained with an Abbe refractometer. Refractive dispersions were obtained from readings on the compensator drum of the same instrument and the accompanying tables. Because of the color of the material, the precision of the refractive indices varies from about ± 0.0003 for the first fractions from the extractors to about ± 0.0001 for the last fractions. In a few cases, where intensity of color caused a lower precision, the values are bracketed. The refractive dispersions are believed to cover about the same range of precision, that is, from ± 0.0003 to ± 0.0001. In the work with the water-white oil [2], values for the Lorentz-Lorenz specific dispersion $(n_F^2-1)/(n_F^2+2) -(n_C^2-1)/(n_C^2+2)\times 1/d$ were computed from the values for n_F-n_C given by the Abbe refractometer. This was done to be consistent, since the Lorentz-Lorenz expression $(n_D^2-1)/(n_D^2+2)\times 1/d$ (desired because of its use in determining the number of naphthene rings per molecule, as described by Vlugter, Waterman, and Van Westen [10]) had been used for the specific refraction. However, since the computation of the Lorentz-Lorenz specific dispersions from n_F-n_C is a tedious process, and since many of the data in the literature are given in terms of the simpler expression of Gladstone and Dale it has been used in this paper.

4. MOLECULAR WEIGHT

Molecular weights were determined by the ebullioscopic method [11], using benzene as the solvent. The results are considered accurate to within ± 1 percent. Many of the samples were too viscous to introduce into the molecular-weight apparatus from a weighing pipette and were not sufficiently solid to add in the form of pellets. Small glass tubes having one end sealed and blown paper-thin were used for the introduction of these samples. Each tube was of such a diameter that it fell easily down the condenser but stuck at a constriction near the bottom of the condenser. The bottom end of the tube was then broken with a strong wire, and, after all the oil had been dissolved by the reflux and washed into the boiler, the remainder of the tube was caught in a hook and withdrawn. The molecular-weight equipment was checked during the course of this work with triphenylmethane. The value obtained for its molecular weight was 242.4, which is to be compared with the theoretical value of 244.3.

5. OPTICAL ROTATION

Both the viscosity and the color of the extraction fractions caused difficulties in the determination of optical rotation. At first, attempts were made to determine the activity of the undiluted oil in a 2-dm tube, as had been done with the water-white oil. However, striations, presumably due to the high viscosity, persisted in the oil and satisfactory fields were not obtained. By dissolving a weighed quantity of 7 to 10 g of the oil in 25 ml of benzene, and by using solutions of this concentration in a 4-dm tube, satisfactory fields were obtained and this procedure was therefore adopted. The high color of the fractions made reading of some fractions difficult with a 4-dm tube, and at the beginning a number of fractions *B–6*, *13*, *15*, *21*, *27*, *31*, *34*, *37–38*, and residue *A–6*, *17*, and residue were distilled in a small molecular still to

remove some of the color. In this distillation the fractions were taken practically to dryness, the greater part of the color being left in the few drops remaining in the still. Since practically the entire sample was distilled over, it is believed that this treatment did not appreciably alter the values for the optical rotation. Later it was found that satisfactory readings could be obtained on most of the samples with the aid of a stronger light source (500 watts). The other rotations were determined on undistilled samples, using a 500-watt bulb when necessary, with the exception of samples *C–4* and *E–8*, which it was felt advisable to distil on account of their very dark color. Determinations of the optical rotation of the distillation key fractions were made on the undiluted oil at 100° F before the technique used for the extraction fractions had been developed. With this method it was not possible to determine optical rotation beyond distillation key fraction 8, either because of the high viscosity or the high color.

To determine whether the optical rotation was the same in benzene solution as in the undiluted oil, readings were made on one of the less viscous samples (*A*-residue) both in the undiluted form and in the form of solution. The values computed for $[\alpha]_D^{20}$ from the undiluted oil and from the solution were $+0.42$ and $+0.44$, respectively. The optical rotations were measured on a saccharimeter in the Polarimetry Section of this Bureau and converted from °S to $[\alpha]_D^{20}$. The values of $[\alpha]_D^{20}$ are believed to be precise to about ± 0.03.[7]

6. BOILING POINT [8]

Boiling points at 1-mm Hg pressure were determined, using a thermocouple calibrated by the Heat Division of this Bureau, in an apparatus which has been described previously [12].

7. ANILINE POINT

Aniline points were determined where possible with 1-ml portions each of oil and freshly distilled dry aniline. The sample was stirred and a slow stream of dry air passed over it. A precision of ± 0.1° C was obtained.

8. SOLUBILITY IN METHYL CYANIDE

Solubilities in methyl cyanide were determined by shaking a slight excess of the oil at about 40° C with methyl cyanide in a 50-ml glass-stoppered Erlenmeyer flask. The flask was then placed in a bath maintained at 25° C and left until the oil which precipitated had settled on the walls and bottom. 25 ml of clear solution was then transferred with a pipette to a 100-ml flask. The bulk of the solvent was removed by distillation and the last traces were pumped off. The gain in weight of the flask gave the weight of oil in 25 ml of solution. The results are believed to be accurate to within ± 0.03 g per 100 ml of solution.

9. CHEMICAL ANALYSIS

(a) CARBON AND HYDROGEN CONTENT

Combustion analyses were performed with the equipment used for the water-white oil [1], modified on account of the presence of sulfur

[7] The authors are indebted to C. F. Snyder and W. W. Pigman for advice and assistance in this work.
[8] The authors are indebted to A. J. Streiff for assistance in this work.

and nitrogen. To remove the oxides of sulfur some of the copper oxide in the exit end of the quartz combustion tube was replaced with lead chromate on copper oxide, as described by Pregl [13]. This section of the furnace was maintained at about 500° C. For samples containing more than 0.05 percent of nitrogen, lead peroxide on asbestos, prepared as described by Pregl [14], was used. This preparation was contained in a separate tube attached to the main quartz combustion tube with a ground joint sealed with Cementyte. The body of the tube containing the lead peroxide was surrounded by a jacket in which *p*-cymene was refluxed, which gave a constant temperature near 176° C. Blank determinations were performed at frequent intervals and corrections usually amounting to about 0.0003 g for the Dehydrite tube and 0.0002 g for the Ascarite tube were necessary. Duplicate determinations were made with 0.5-g samples. The arithmetical average of the differences between duplicate determinations of the ratio moles H_2O/CO_2 was ±6 parts in 10,000, exclusive of fraction *A–27*, for which the difference was ±39 parts in 10,000. An uncertainty of 6 parts in 10,000 in the mass of water, or of carbon dioxide, corresponds to an uncertainty of about 0.006 percent by weight of hydrogen in the sample or about 0.05 percent by weight of carbon.

As a check on the accuracy of the combustion analyses, experiments were performed with known mixtures of cystine ($C_6H_{12}O_4S_2N_2$) and *n*-nonacosane ($C_{29}H_{60}$), the data for which are given in table 8.

Although the agreement between the values calculated and those found for the ratio moles H_2O/CO_2 is not very satisfactory, some of this difference may be due to impurities in the cystine. The agreement between the mass of the sample minus the mass of carbon plus hydrogen calculated and that found is reasonably satisfactory, and shows that the percentage of elements other than carbon and hydrogen in the oil samples may be calculated with an accuracy of about 0.04 percent by weight.

TABLE 8.—*Results which illustrate the accuracy of the combustion analyses*

Experiment	Nonacosane	Cystine	Ratio: Moles H_2O/CO_2		Mass of sample, less mass of C+H	
			Calculated	Found	Calculated	Found
	g	*g*			*Percent by weight*	*Percent by weight*
1	0.5014	0.0517	1.0333	1.0378	6.07	6.11
2	.5020	.0517	1.0333	1.0372	6.07	6.10

(b) SULFUR, NITROGEN, AND OXYGEN CONTENT[5]

The sulfur analyses were made by a method described by C. E. Waters [15]. The nitrogen was determined by the Kjeldahl method, using mercuric acetate as a catalyst with the addition of potassium sulfate. After digestion, the ammonia was distilled in a current of steam into *N*/100 HCl. The excess acid was titrated with *N*/100 NaOH, using methyl red as an indicator, with the solution at its boiling point.

[5] The authors are indebted to C. E. Waters for the sulfur determinations and to C. J. Rodden for the determinations of nitrogen.

The percentage of oxygen was obtained by subtracting the sum of the percentages of carbon, hydrogen, sulfur, and nitrogen from 100.

IX. TABULATION OF RESULTS

In table 9 are tabulated the kinematic viscosities at 100° and 210° F, the refractive indices, densities, refractive dispersions, specific rotations, and aniline points of many of the fractions from extractors *A*, *B*, *C*, *D*, and *E*. Data on the solubility of a few of the fractions in methyl cyanide are also given. Three derived quantities, kinematic-viscosity index, specific refraction, and specific dispersion, are also included in this table.

TABLE 9.—*Properties of fractions from final extraction process*

TABLE 9.—*Properties of fractions from final extraction process*

Fraction [a]	Percentage extracted [b]	Kinematic viscosity [c] at 100° F	Kinematic viscosity at 210° F	Kinematic viscosity index	Refractive index [d] n_D^{25}	Density at 25° C [e]	Refractive dispersion $n_F - n_C$ at 25° C	Specific optical rotation $[\alpha]_D^{29}$	Aniline point	Solubility in methyl cyanide at 25° C	Specific refraction [f] $\frac{n^2-1}{n^2+2} \times \frac{1}{d}$	Specific dispersion [f] $\frac{n_F - n_C}{d}$
Series *A*. Charge =581 g. Boiling-point range at 1 mm Hg=180.4° to 189.4° C												
Original charge [a]		*Stokes* 0.75 to 1.30	*Stokes* 0.060 to 0.075	(−108)	(1.561)	*g/ml* (0.983)	(0.0197)	(+0.27)	°C (9)	*g/ml of solution*	(0.329)	(0.0200)
[1]	8.6	5.00	0.0940	−634	1.6305	1.063				8.98	.3350	
2	11.6	3.87	.0856	−584	1.6317							
3	17.4	4.12	.0884	−578	1.6302							
4	23.4	3.99	.0882	−557	1.6202						.3322	.0251
[5]	28.3	3.97	.0903	−514	1.6095	1.043	.0262			3.66		
6	31.5	3.96	.0943	−447	1.5995						.3307	.0230
7	34.6	3.85	.0930	−447	1.5949	1.027	.0236					
8	37.4	3.71	.0950	−394	1.5897							
9	40.5	3.75	.0967	−378	1.5840						.3294	.0210
[10]	43.3	3.43	.0946	−352	1.5798	1.010	.0212	+.13				
11	46.0	3.13	.0939	−307	1.5746							
12	48.8	2.85	.0954	−243	1.5706				−5.2			
13	51.8	2.39	.0896	−219	1.5633							
14	54.4	2.16	.0872	−198	1.5578	.9861	.0174		+5.1		.3268	.0176
15	57.0	2.03	.0870	−173	1.5532							
16	59.5	1.65	.0824	−133	1.5465							
[17]	62.2	1.29	.0763	−97	1.5389	.9660	.0144	+.49	+18.0		.3242	.0149
18	64.7	1.16	.0743	−77	1.5344							
19	67.2	1.01	.0711	−59	1.5290							
20	69.6	.877	.0678	−42	1.5256	.9496	.0127		25.8	1.75	.3230	.0134
21	72.3	.714	.0640	−12	1.5215							
[22]	75.1	.620	.0602	−3	1.5188	.9363	.0121		31.3		.3241	.0129
23	77.4	.581	.0581	−3	1.5165							
24	79.9	.500	.0554	+17	1.5135							
25	82.3	.452	.0531	+25	1.5110	.9219	.0118	+.36	37.0		.3250	.0128
26	85.2	.400	.0508	+38	1.5076							
[27]	87.6	.362	.0496	+55	1.5058	.9097	.0115		39.7		.3265	.0126
28	90.0	.334	.0476	+58	1.5020	.9035	.0111	+.16	46.6	.95	.3266	.0123
29+30	92.7	.327	.0483	+71	1.4961	.8959	.0103		60.6		.3261	.0115
31+32	94.7	.305	.0471	+78	1.4837	.8818	.0087		84.8	*	.3243	.0099
33	95.8				1.4745			+.76	97.5			
[Res.]	100	.188	.0395	+137	1.4654	.8448	.0083	+.44	104.9	.09	.3275	.0098

See footnotes at end of table.

TABLE 9.—*Properties of fractions from final extraction process*—Continued

Fraction [a]	Percentage extracted [b]	Kinematic viscosity [c] at 100° F	Kinematic viscosity at 210° F	Kinematic viscosity index	Refractive index [d] n_D^{25}	Density at 25° C [e]	Refractive dispersion $n_F - n_C$ at 25° C	Specific optical rotation $[\alpha]_D^{20}$	Aniline point	Solubility in methyl cyanide at 25° C	Specific refraction [f] $\frac{n^2-1}{n^2+2}\times\frac{1}{d}$	Specific dispersion [f] $\frac{n_F-n_C}{d}$
Series *B*. Charge=605 g. Boiling-point range at 1 mm Hg=1.98.4° to 204° C												
		Stokes	*Stokes*			*g/ml*			°C	*g/ml of solution*		
Original charge [g]		1.9 to 2.8	0.090 to 0.104	(−151)	(1.564)	(0.989)	(0.0201)	(+0.49)	(15)		(0.329)	(0.0203)
1	2.4	36.2	0.170	−1590	1.6387							
[2]	7.6	26.7	.153	−1420	1.5397	1.071					.3362	
3	11.0	21.6	.148	−1210	1.6397							
4	14.8	19.6	.145	−1130	1.6368							
5	18.1	18.9	.144	−1100	1.6332							
[6]	21.4	18.7	.146	−1050	1.6306	1.061	.0300	−.02			.3355	.0283
7	23.7	(16.1)			1.6256							
8	25.8	16.9			1.6212	1.055	.0269				.3335	.0255
9	28.1	16.0	.150	−813	1.6155							
10	30.5	14.6	.157	−642	1.6098	1.045					.3316	
11	33.7	13.0	.150	−623	1.6016	1.037	.0246				.3307	.0237
12	36.4	12.0	.150	−560	1.5952	1.030	.0236				.3299	.0229
[13]	39.5	11.9	.151	−543	1.5903	1.026	.0222	+.30			.3292	.0216
[14]	42.1	10.5	.149	−473	1.5834	1.019	.0218				.3282	.0214
15	44.5	9.71	.149	−422	1.5820	1.016	.0211	+.36			.3286	.0208
16	47.2	8.31	.144	−369	1.5785	1.010	.0207		−3.5		.3287	.0205
17	49.8	6.95	.138	−318	1.5732	1.004	.0200				.3285	.0199
[18]	52.4	6.58	.34	−320	1.5695	0.9990	.0193	+.52	4.1		.3282	.0193
19	54.8	5.60	.130	−269	1.5652	.9942	.0187				.3277	.0188
20	57.4	4.74	.126	−221	1.5601	.9884	.0179				.3272	.0181
[21]	60.1	4.19	.123	−189	1.5558	.9837	.0173	+.80	13.0		.3267	.0176
22	62.9	3.19	.113	−148	1.5496	.9762	.0166				.3261	.0170
23	65.1	2.92	.111	−129	1.5466		.0159		20.2			
24	67.2	2.54	.106	−111	1.5416	.9673	.0150	+1.09	23.7		.3252	.0155
25	69.4	2.20	.103	−82	1.5349	.9613	.0139		27.0		.3238	.0145
26	71.0	1.73			1.5305	.9541	.0136		31.5		.3240	.0143
27	73.1	1.53	.0897	−51	1.5276	.9485	.0131	+1.10	34.1		.3244	.0138
[28]	74.8	1.24	.0843	−24	1.5229	.9439	.0125	+.97	36.5		.3236	.0132
29	77.1	1.08	.0793	−17	1.5196	.9388	.0123		39.2		.3235	.0131
30	79.0	0.925	.0744	−7	1.5168	.9336	.0120				.3240	.0129
[31]	81.2	.786	.0711	15	1.5141	.9278	.0118	+.68	44.2		.3245	.0127
32	83.3	.689	.0673	24	1.5110	.9232	.0115				.3245	.0125

30	79.0	0.925	.0744	−7	1.5168	.9336	.0120				.3240	.0129
[31]	81.2	.786	.0711	15	1.5141	.9278	.0118	+.68	44.2		.3245	.0127
32	83.3	.689	.0673	24	1.5110	.9232	.0115				.3245	.0125
33	85.4	.599	.0637	35	1.5089	.9177	.0117		47.0		.3253	.0127
34	88.0	.516	.0602	48	1.5060		.0115	+.41				
[35]	90.1	.456	.0575	59	1.5027	.9051	.0112		51.3		.3265	.0124
36	92.2	.437	.0572	68	1.4999	.9005	.0110	+.27	55.3		.3266	.0122
37+38	94.5	.563	.0647	57	1.4930	.8976	.0092	+1.94	79.2		.3238	.0103
[Res.]	100	.309	.0506	104	1.4723	.8594	.0087	+1.31	106.0		.3260	.0101

Series *C*. Charge=666 g. Boiling-point range 1 mm Hg=214° to 218° C

Original charge[a]		4.4 to 5.2	0.128 to 0.141	(−171)	(1.564)	(0.989)	(0.0200)	+(0.65)	(21)		(0.329)	(0.0202)
[1]	5.2		.340		(1.641)	1.076					.3353	
2	9.0	248	.311	−3350	1.6407							
3	12.3	158	.284	−2520	1.6366							
4	15.3	106	.275	−1750	1.6314			+.19				
[5]	17.9	97.8	.264	−1750	1.6278	1.061	.0298				.3343	.0281
6	20.6	84.1	.258	−1560	1.6248							
7	23.9	70.3	.253	−1340	1.6189							
[8]	26.9	56.2	.246	−1100	1.6126							
9	29.6	47.8	.241	−958	1.6081	1.041	.0264				.3321	.0254
10	32.0	42.3	.241	−827	1.6048		.0259					
11	34.6	36.8	.234	−750	1.5993	1.034	.0244	+.41			.3306	.0236
[12]	37.3	32.9	.230	−682	1.5952	1.029	(.0241)				.3304	.0234
13	39.9	29.8	.229	−606	1.5911	1.025	.0234				.3298	.0228
14	42.5	26.6	.219	−586	1.5863	1.020	.0222				.3293	.0218
15	45.0	23.7	.213	−542	1.5822	1.015	.0212				.3288	.0209
16	47.4	20.2	.212	−440	1.5787	1.011	.0209	+.65	1.6		.3285	.0207
[17]	49.9	15.6	.201	−351	1.5733	1.005			6.1		.3281	
18	52.4	13.4	.194	−308	1.5699	1.000	.0195		8.5		.3280	.0195
19	55.0	11.0	.184	−264	1.5651	0.9944	.0189				.3276	.0190
20	57.2	9.87	.182	−223	1.5622	.9909			14.4		.3274	
21	59.4	8.29	.173	−195	1.5580	.9865	.0178				.3268	.0180
[22]	61.4	7.61	.166	−193	1.5554	.9827	.0167		18.5		.3268	.0170
23	63.3	6.40	.163	−143	1.5516	.9787	.0166	+1.11	21.4		.3263	.0170
[24]	64.9	5.63	.153	−141	1.5487	.9757	.0162		23.4		.3259	.0166
25	66.7	4.14	.138	−105	1.5407	.9666	.0154	+1.16	30.2		.3249	.0159
26	68.5	3.19	.130	−61	1.5347	.9576	.0144	+1.14	34.9		.3250	.0150
27	70.3	2.78	.121	−61	1.5303	.9542	.0137		36.5		.3239	.0144
[28]	72.3	2.18	.113	−30	1.5264	.9479	.0132		40.7	0.76	.3240	.0139
29	74.1	1.96	.106	−34	1.5236	.9440	.0128	+0.94			.3239	.0136
30	75.9	1.72	.103	−14	1.5215	.9403	.0125		44.2		.3241	.0133

See footnotes at end of table.

TABLE 9.—*Properties of fractions from final extraction process*—Continued

Fraction [a]	Percentage extracted [b]	Kinematic viscosity [c] at 100° F	Kinematic viscosity at 210° F	Kinematic viscosity index	Refractive index [d] n_D^{25}	Density at 25° C [e]	Refractive dispersion $n_F - n_C$ at 25° C	Specific optical rotation $[\alpha]_D^{20}$	Aniline point	Solubility in methyl cyanide at 25° C	Specific refraction [f] $\frac{n^2-1}{n^2+2}\times\frac{1}{d}$	Specific dispersion [f] $\frac{n_F-n_C}{d}$
Series *C*. Charge=666 g. Boiling-point range 1 mm Hg=214° to 218° C—Continued												
		Stokes	*Stokes*			*g/ml*			°C	*g/ml of solution*		
31	77.9	1.46	.0971	0	1.5180	.9348	.0123	+.87			.3242	.0132
[32]	80.3	1.22	.0908	14	1.5152	.9287	.0118		48.1		.3248	.0127
33	82.5	1.01	.0806	8	1.5111	.9230	.0117				.3246	.0127
34	84.5	0.863	.0785	35	1.5083	.9177	.0113	+.49			.3250	.0123
35	86.7	.738	.0752	53	1.5056	.9124	.0112		55.9		.3254	.0123
[36]	88.9	.622	.0714	70	1.5023	.9058	.0116	+.30			.3260	.0128
37	91.2	.570	.0674	69	1.4993	.8996	.0106	+.38	62.4		.3266	.0118
38	92.4				1.4942	.8970	.0099	+1.63	77.5		.3247	.0110
[39+40]	94.8	.907	.0845	51	1.4896	.8958	.0087	+2.97	93.6		.3225	.0097
41	96.3	.631	.0716	68	1.4797	.8774	.0084	+2.14	105.4		.3236	.0096
[Res]	100	.364	.0579	112	1.4711	.8560	.0082	+.81	111.1		.3266	.0096
Series *D*. Charge=573 g. Boiling-point range at 1 mm Hg=232.4° to 237.4° C.												
Original charge [g]		14 to 16	0.19 to 0.21	(−155)	(1.563)	(0.989)	(0.0198)	+(0.59)	(29)		(0.328)	(0.0200)
[1]	9.4		0.921		(1.6350)	1.071					.3343	
2	15.8		.660		(1.6270)							
3	18.7		.542		1.6190					2.89		
4	21.2	395	.505	−1,990	1.6143							
5	24.0	289	.481	−1,570	1.6118							
6	27.1	229	.458	−1,350	1.6087							
7	29.6	177	.436	−1,120	1.6053	1.039	.0264				33.16	.0254
8	32.2	136	.410	−952	1.6007							
9	34.6	115	.394	−856	1.5997		.0238	+.50				
10	37.8	82.3	.365	−684	1.5928							
[11]	41.1	67.2	.359	−551	1.5884	1.022	.0227		<−10		.3296	.0222
12	44.2	52.1	.335	−470	1.5842							
13	47.3	40.9	.316	−394	1.5797	1.010	.0201		8.8		.3292	.0199
14	50.4	34.7	.302	−352	1.5752							
15	53.4	27.9	.285	−300	1.5697					1.09		

[16]	56.1	24.0	.279	−251	1.5658	0.9959	.0180		17.4		.3274	.0181
17	58.7	17.7			1.5596							
18	61.0	12.7	.234	−140	1.5553		.0172	+.83	25.9			
19	63.4	9.55	.211	−113	1.5491	.9742	.0163		30.8		.3266	.0167
20	66.1	6.99	.190	−80	1.5427				36.6			
21	68.4	5.44	.174	−58	1.5369							
22	70.6	4.40	.161	−42	1.5315	.9530	.0139	+.65	43.8	.50	.3249	.0146
23	72.9	3.68	.152	−25	1.5277		.0134					
24	75.1	2.98	.141	−8	1.5228		.0125					
[25]	77.6	2.36	.129	7	1.5185	.9344	.0120		54.1		.3246	.0128
26	79.7	1.96	.120	19	1.5144	.9296	.0116		56.8		.3241	.0125
27	81.6	1.66	.113	30	1.5115	.9249	.0113	+.54	59.1		.3242	.0122
[28+29]	85.5	1.29	.101	42	1.5069	.9157	.0112		63.1		.3249	.0122
30	87.9	.994	.0918	60	1.5032	.9083	.0110		65.6	.25	.3256	.0121
31	90.7	.890	.0892	71	1.4998	.9021	.0105	+.50			.3259	.0116
32+33	93.8	1.214	.1028	58	1.4903	.8948	.0093	+2.14	96.7		.3233	.0104
34	95.9	.708	.0814	86	1.4774	.8702	.0084		112.5		.3249	.0097
Res.]	100	.457	.0686	115	1.4707	.8539	.0082	+.40	116.2	.03	.3272	.0096

Series *E*. Charge=514 g. Boiling-point range at 1 mm Hg=251.4° to 258.2° C

Original charge		19.4 to 26.3	0.291 to 0.335	(−155)	(1.563)	(0.989)	(0.0197)		(37)		(0.328)	(0.0199)
[1]	8.8					1.074						
2	11.7		1.82		(1.627)							
3	14.4		1.54		(1.622)							
4	17.3		1.55		(1.620)							
5	20.3		1.41		(1.617)							
6	22.5				(1.613)							
7	26.0		1.09		(1.610)							
[8]	29.9		.935		1.6057	1.039	.0255	+0.72		1.52	.3318	.0245
9	32.6	886	.892		1.6025							
10	35.7	576	.813		1.5990							
11	38.7	406	.758		1.5947							
12	41.3	313	.684		1.5900							
[13]	44.3	189	.599	−584	1.5858	1.018			(1.8)	.94	.3296	
14	47.0	149	.570	−486	1.5827							
15	49.2				1.5783							
16	51.8	68.8	.471	−271	1.5719	1.003	.0199		21.1		.3281	.0199
17	54.5	47.4	.425	−202	1.5667							
18	57.3	36.3	.398	−154	1.5617	.9906	.0182		28.1		.3272	.0184
19	59.9	30.6	.371	−142	1.5581							
20	62.4	26.0			1.5547							

See footnotes at end of table.

TABLE 9.—*Properties of fractions from final extraction process*—Continued

Fraction [a]	Percentage extracted [b]	Kinematic viscosity [c] at 100° F	Kinematic viscosity [c] at 210° F	Kinematic viscosity index	Refractive index [d] n_D^{25}	Density at 25° C [e]	Refractive dispersion $n_F - n_C$ at 25° C	Specific optical rotation $[\alpha]_D^{25}$	Aniline point	Solubility in methyl cyanide at 25° C	Specific refraction [f] $\frac{n^2-1}{n^2+2}\times\frac{1}{d}$	Specific dispersion [f] $\frac{n_F-n_C}{d}$
Series *E*. Charge=514 g. Boiling-point range at 1 mm Hg=251.4° to 258.2° C—Continued												
		Stokes	*Stokes*			*g/ml*			*°C*	*g/ml of solution*		
[21]	65.6	15.5	0.289	−83	1.5491	0.9724	0.0163		37.6	0.45	0.3272	0.0168
22	68.4	12.0	.274	−46	1.5435	.9665	.0157		41.2		.3264	.0162
23	70.6				1.5351							
24	72.6	8.15			1.5299	.9542	.0132		50.0		.3237	.0138
25	75.3	4.51	.187	10	1.5210							
26	77.6	3.56	.171	24	1.5159	.9321	.0117	+.84	63.0		.3240	.0126
[27]	81.6	2.36	.143	41	1.5093	.9203	.0112		68.6	.14	.3246	.0122
28	84.1	2.02	.136	52	1.5065	.9163	.0109				.3245	.0119
29	86.4	1.83	.134	63	1.5050	.9140	.0108		72.7		.3245	.0118
30	88.7	1.43	.122	77	1.5005	.9045	.0106	+.32			.3254	.0117
31+32	92.9	1.54	.125	72	1.4904	.8924	.0090	+1.12	100.1		.3242	.0101
33	95.3	.984	.102	89	1.4776	.8703	.0086		116.9		.3250	.0099
34	97.2	.774			1.4740							
[Res.]	100.0	.659	.0865	111	1.4724	.8560	.0087	+.42	121.6	.02	.3274	.0102

[a] The brackets indicate key fractions on which additional data are given in table 10.

[b] The size of each fraction is given in terms of its location on a scale of 0 to 100 percent for the charge. Fraction *E-2*, for example, constitutes that part of the original charge coming from the extractor at 8.8 to 11.7 percent.

[c] The actual temperatures of these determinations, as measured with a platinum resistance thermometer, were 99.9° and 210.1° F., respectively.

[d] The values of the refractive indices may be converted to other temperatures by using for dn_D/dt the value 0.00038/° C. Over a 5-degree interval this conversion will not introduce an uncertainty greater than ±0.0002, which is, in most cases, about the experimental accuracy.

[e] The values of the density may be converted to other temperatures by using for dD/dt the value 0.0007 g/ml/° C. Over a 5-degree interval this conversion will not introduce an uncertainty greater than ±0.0003 g/ml, which is about the experimental accuracy.

[f] The values for the specific refraction and specific dispersion may be regarded as constant over a 5-degree range of temperature within the accuracy of these measurements.

[g] The properties of the original charge recorded in parentheses were obtained by interpolation from the distillation keys given in table 6.

In table 10 additional data are recorded on 41 key fractions. These data include boiling points, molecular weights, carbon and hydrogen contents, percentages of sulfur plus nitrogen plus oxygen, and the calculated quantities n and x in the formula C_nH_{2n+x}. For some of the fractions, the percentages of sulfur, nitrogen, and oxygen are recorded.

TABLE 10.—*Additional properties of key fractions from final extraction process*

Fraction	Boiling point at 1 mm Hg	Molecular weight	Combustion analyses		Sulfur content [b]	Nitrogen content [b]	Oxygen content [c]	In the formula $C_nH_{2n+z}S_yN_xO_w$				
			Ratio: moles H_2O/CO_2	Mass of sample less mass of C+H				n	z	y	x	w
			SERIES *A*									
	°C			% by wt of sample		% by wt						
Original charge [a]	(185)	(300)	(0.686)	(1.3)	(0.8)	(0.03)	(0.5)	(22.1)	(−13.7)	(0.08)	(0.01)	(0.09)
A-1	185	269	.5397	2.61	1.22	.13	1.26	20.0	−18.42	.10	.02	.21
A-5	186	282	.5792	2.50	1.73	.01	0.76	20.9	−17.56	.15	.00	.13
A-10		298	.6445	1.58	0.92	.01	.65	22.0	−15.65	.09	.00	.12
A-17		318	.7351	0.85	.36	(.01)	.48	23.3	−12.37	.04	.00	.10
A-22	185	329	.7824	.55	.25	.01	.29	24.1	−10.47	.03	.00	.06
A-27	189	348	(.8130)	.67	.28	(.00)	.28	25.4	−9.48	.03	.00	.06
A-res	187	357	.9746	(.69)				25.3	−1.29			
			SERIES *B*									
Original charge [a]	(201)	(325)	(0.686)	(1.4)	(0.9)	(0.04)	(0.5)	(23.9)	(−14.9)	(0.09)	(0.01)	(0.10)
B-2	200	281	.5283	2.12				21.0	−19.84			
B-6	202	288	.5521	2.49				21.4	−19.18			
B-13	202	311	.6183	2.29				22.9	−17.51			
B-14		313	.6377	2.13				23.0	−16.68			
B-18		326	.6730	1.43				24.0	−15.71			
B-21	202	330	.7040	0.91				24.4	−14.42			
B-28		354	.7819	.63				25.9	−11.30			
B-31	201	360	.8037	.57				26.3	−10.31			
B-35		366	.8332	.59				26.6	−8.87			
B-res	203	383	.9586	.16				27.4	−2.27			

SERIES *C*

SERIES C

Original charge [a]	(216)	(347)	(0.691)	(1.4)	(0.9)	(0.06)	(0.4)	(25.5)	(−15.7)	(0.10)	(0.01)	(0.09)
C-1	218	303	.5363	2.63	.77	.56	1.30	22.5	−20.90	.07	.12	.25
C-5	217	312	.5632	2.36	1.49	.08	0.79	23.2	−20.27	.14	.02	.15
C-8		321	.5920	2.42				23.7	−19.35			
C-12	217	329	.6249	2.24	1.50	.02	.72	24.3	−18.21	.15	.00	.15
C-17	216	337	.6708	1.74	(1.1)	(.01)	(.60)	24.8	−16.31	(.10)	.00	(.13)
C-22	217	354	.7128	1.17	0.72	.01	.44	26.0	−14.95	.08	.00	.10
C-24		362	.7269	1.33				26.5	−14.48			
C-28		378	.7793	0.90	.43	(.01)	.47	27.6	−12.19	.05	.00	.11
C-32	215	390	.8073	.60	.31	(.01)	.28	28.5	−10.97	.04	.00	.07
C-36		395	.8392	.79	.37	(.01)	.33	28.7	−9.22	.05	.00	.07
C-39+40	216	412	.9115	.37	.17	.01	.19	29.6	−5.24	.02	.00	.05
C-res	219	420	.9696	.02	(.01)	(.00)	(.01)	30.1	−1.83	.00	.00	.00

SERIES D

Original charge [a]	(235)	(377)	(0.706)	(1.5)	(0.9)	(0.09)	(0.5)	(27.6)	(−16.2)	(0.11)	(0.02)	(0.12)
D-1		321	.5585	2.66				23.8	−21.04			
D-11	237	361	.6474	2.48				26.4	−18.64			
D-16	235	379	.6919	2.00				27.7	−17.06			
D-25	234	414	.8060	(1.01)				30.1	−11.67			
D-38+39	235	430	.8355	0.64				31.2	−10.26			
D-res	238	457	.9739	.22				32.6	−1.70			

SERIES E

Original charge [a]	(255)	(415)	(0.712)	(1.6)	(0.9)	(0.13)	(0.6)	(30.5)	(−17.6)	(0.12)	(0.04)	(0.15)
E-1		367	.5666	2.98	.81	.71	1.46	27.1	−23.46	.09	.19	.33
E-8		394	.6249	2.42	(1.3)	.09	(1.03)	29.0	−21.77	(.16)	.03	(.25)
E-18	260	409	.6609	2.15	1.30	.06	0.79	30.0	−20.33	.17	.00	.20
E-21	257	436	.7387	1.44	0.85	.03	.56	31.9	−16.65	.12	.00	.15
E-27	255	469	.8348	0.62	.36	(.01)	.25	34.0	−11.25	.05	.00	.07
E-res	263	496	.9714	.08				35.5	−2.03	.00	.00	.00

[a] The properties of the original charge given in parentheses were obtained by interpolation from the distillation keys given in table 6.
[b] The values in parentheses in these columns were estimated.
[c] The percentage of oxygen was obtained by subtracting the sum of the percentages of carbon, hydrogen, sulfur, and nitrogen from 100.

X. SUMMARY

Although a more complete interpretation of these data in terms of the chemical constitution will follow in a subsequent paper, a few of the more obvious facts may be pointed out here. The extremely wide range in physical properties between the first and last fractions, obtained from the extraction of substantially constant-boiling fractions, is obvious.

The kinematic viscosity at 100° F varies from 248 stokes for fraction *C–2* to 0.36 stoke for *C*-residue, while the viscosity indices for the same fractions vary from −3,350 to +112. A small maximum occurs for the viscosity index at fractions 36 and 37, and a minimum for the viscosity at fraction 37.

Refractive indices vary from 1.641 to 1.4711 and densities from 1.076 to 0.8560. Dispersions vary from 0.0298 for *C–5* to 0.0096 for *C*-residue.

Optical rotations show interesting maxima and minima. The optical rotation $[\alpha]_D^{20}$, increases from +0.19 for *C–4* to a maximum of +1.16 at *C–25*, then decreases to a minimum of +0.30 for *C–36*, rises again to a maximum of +2.97 for *C–39+40*, and finally decreases to a minimum of +0.81 for the residue. Maxima and minima are also observed for the specific refractions.

Aniline points increase from 1.6° C for *C–16* to 111.1° C for *C*-residue.

Although the boiling points are substantially constant for the fractions from any one series there is a marked increase in molecular weights. For example, for series *C*, the molecular weights for the first and last fractions are 303 and 420, respectively.

The hydrogen content increases from *C–1* to *C*-residue, the values for the ratio moles H_2O/CO_2 being 0.5363 and 0.9696, respectively. The values for x in the equation C_nH_{2n+x} increase from $x=-20.9$ for *C–1* to −1.83 for *C*-residue. It is interesting to note that sulfur is not concentrated in the first fractions but increases from 0.77 percent for *C–1* to a maximum of 1.50 percent in the region from *C–5* to *C–12* and then decreases to 0.31 for *C–32*. A slight increase to 0.37 percent for *C–36* then occurs. The nitrogenous material, on the other hand, is concentrated in the first few fractions, being 0.56 percent for *C–1*, 0.08 percent for *C–5*, and not greater than 0.01 percent for all the fractions beyond about the twelfth.

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HYDROGENATION OF THE "EXTRACT" PORTION OF THE LUBRICANT FRACTION FROM A MIDCONTINENT PETROLEUM [1] *

By Beveridge J. Mair, Charles B. Willingham, and Anton J. Streiff [2]

ABSTRACT

To obtain information about the chemical constitution of the extract portion of the lubricant fraction from a midcontinent petroleum, fifteen selected fractions, prepared by extensive distillation and extraction, were completely hydrogenated. The hydrogenation procedure is described and there are tabulated and compared values for the physical constants of the fractions before and after hydrogenation. Evidence is presented to show that, under the conditions of these experiments, namely, temperatures from 230° to 250° C and pressures of hydrogen from 170 to 210 atm, the fractions were completely hydrogenated and that no break-down of the molecules occurred.

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I. INTRODUCTION

That hydrogenation is a powerful tool for investigating the chemical composition of lubricating oil fractions has been demonstrated by Vlugter, Waterman, and Van Westen [1].[3] More recently the method has been used by Müller and Neyman-Pilat [2]. By controlled hydrogenation, these authors convert practically completely the aromatic rings into hydroaromatic or naphthenic rings, without breaking down the molecule. By measuring the hydrogen consumed in the

[1] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of Project 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

[2] Research Associates at the National Bureau of Standards, representing the American Petroleum Institute.

[3] Figures in brackets indicate the literature references at the end of this paper.

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process, or by determining the x value in the formula C_nH_{2n+x} before and after hydrogenation, it is possible with certain reasonable assumptions to compute the average number of aromatic rings in the original fraction.

In an investigation [3] of the composition of the extract portion of the lubricant fraction from a midcontinent petroleum, there were prepared in this laboratory five series of fractions which are believed to be more nearly homogeneous with respect to size and type of molecule than any fractions hitherto obtained from the extract portion of the lubricant fraction of any petroleum.

The source of these fractions is shown graphically in figure 1. They were prepared from the extract portion of the lubricant fraction

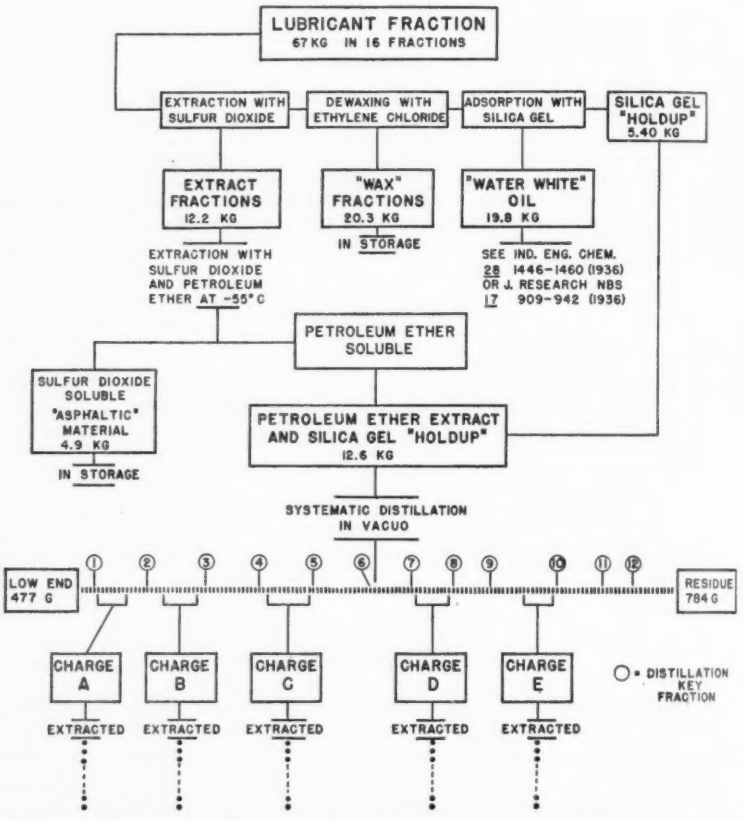
LUBRICANT FRACTION
67 KG IN 16 FRACTIONS
EXTRACTION WITH SULFUR DIOXIDE
DEWAXING WITH ETHYLENE CHLORIDE
ADSORPTION WITH SILICA GEL
SILICA GEL "HOLDUP" 5.40 KG
EXTRACT FRACTIONS 12.2 KG
"WAX" FRACTIONS 20.3 KG
"WATER WHITE" OIL 19.8 KG
IN STORAGE
EXTRACTION WITH SULFUR DIOXIDE AND PETROLEUM ETHER AT −55° C
SEE IND. ENG. CHEM. 28 1446–1460 (1936) OR J. RESEARCH NBS 17 909–942 (1936)
PETROLEUM ETHER SOLUBLE
SULFUR DIOXIDE SOLUBLE "ASPHALTIC" MATERIAL 4.9 KG
IN STORAGE
PETROLEUM ETHER EXTRACT AND SILICA GEL "HOLDUP" 12.6 KG
SYSTEMATIC DISTILLATION IN VACUO
LOW END 477 G
RESIDUE 784 G
CHARGE A
CHARGE B
CHARGE C
CHARGE D
CHARGE E
EXTRACTED
DISTILLATION KEY FRACTION

FIGURE 1.—*Chart showing treatment and disposition of lubricating-oil fractions.*

of a midcontinent petroleum by extensive distillation followed by the exhaustive extraction of charges with narrow-boiling ranges in 16.7-m columns, using methyl cyanide or a mixture of methyl cyanide and acetone as a solvent. In correlating the large number of physical data which had been obtained on these extraction fractions, it became evident that a direct determination of the number of aromatic rings per molecule by the hydrogenation method would be of great value

in interpreting the physical properties of these fractions in terms of their chemical constitution. Furthermore, the hydrogenation process would yield naphthenic fractions with several rings per molecule whose physical properties would also be of value in this correlation.

This paper describes the method employed in hydrogenating 15 of these extraction fractions and tabulates for comparison the physical properties of the fractions before and after hydrogenation. The fractions which were hydrogenated resulted from the extraction of series *B*, *C*, and *E* (fig. 1). Their position in the extraction series is recorded in table 2.

II. HYDROGENATION EQUIPMENT

Hydrogenation equipment, complete with bomb with thermocouple well, heating and shaking devices, and gages similar to that described by Adkins [4] was used.[4] The volumes of the bomb and copper liner were 500 and 350 ml, respectively. Two hydrogen cylinders were used. The bomb was first charged by the more nearly exhausted cylinder and finally by a full or nearly full cylinder, so that the initial pressure at room temperature was always above 100 atm.

III. PRELIMINARY HYDROGENATION EXPERIMENTS AND CATALYSTS USED

The experience gained in the preliminary experiments, the results of which are recorded in table 1, determined the procedure adopted. These experiments were performed at temperatures of 230° to 250° C and at pressures of from 170 to 210 atm of hydrogen and the time of each treatment was from 10 to 12 hours. It should be noted that the fractions contained considerable quantities of sulfur and oxygen and one contained 0.71 percent of nitrogen.

[4] This equipment was purchased from the American Instrument Co., Silver Spring, Md.

TABLE 1.—*Results of experiments in the hydrogenation of oil fractions*

(Temperatures, 230° to 250° C; hydrogen pressure, 170 to 210 atm; time per hydrogenation, 10 to 12 hours)

Catalyst [a]	Number of treatments with hydrogen	Refractive index n_D^{25}	Refractive dispersion $n_F - n_C$ at 25° C	Sulfur [b] content	Nitrogen [b] content	Oxygen [b] content	Remarks	Solvent and amount used
				FRACTION *C-20* (14 g)				
g				*Percent by wt*	*Percent by wt*	*Percent by wt*		*ml*
	0	1.5622	0.0183	(0.0)	(0.01)	(0.53)		None.
3 Ni-K	1	1.5571	.0178					Do.
3 Ni-K	2	1.5470	.0158					Do.
3 Ni-K	3	1.5402						Do.
3 Ni-K	4	1.5369	.0139					Do.
10 Ni-K	5	1.5295	.0130					75—*n*-heptane.
10 Ni-K	6	1.5084	.0103					Do.
10 Ni-K	7	1.5005	.0092					Do.
				FRACTION *C-13* (17 g)				
	0	1.5911	0.0234	(1.4)	(0.02)	(0.7)		
10 Ni-K	1	1.5762	.0209				NiS formed	75—*n*-heptane.
7 Ni-R	2	1.5554	.0170				do	Do.
15 Ni-R	3	1.5201	.0113				do	Do.
15 Ni-R	4	1.5062	.0096				do	Do.
15 Ni-R	5	1.5047	.0092				Trace of NiS formed	Do.

FRACTION C-7 (20 g)

FRACTION C-7 (20 g)

	0	1.6189	(0.0281)	(1.5)	(0.05)	(0.8)		
50 Ni-R	1	1.5442	.0142				NiS formed	75—*n*-heptane.
45 Ni-R	2	1.5228	.0113				No NiS formed	75—methylcyclohexane.
40 Ni-R	3	1.5175	.0106				do	Do.
30 Ni-R	4	1.5079	.0097				do	Do.
25 Ni-R	5	1.5059	.0093				do	Do.

FRACTION E-1 (32 g)

	0	(1.63)	(0.030)	0.81	0.71	1.46		
45 Ni-R	1	1.5677						75—methylcyclohexane.
45 Ni-R	2	1.5348	.0127				Ammonia formed	Do.
45 Ni-R	3	1.5218	.0110				do	Do.
40 Ni-R	4	1.5189	.0106				do	Do.
45 Ni-R	5	1.5162	.0103				do	Do.
40 Ni-R	6	1.5138	.0101				do	Do.
40 Ni-R	7	1.5122	.0100				Trace of ammonia formed	Do.
45 Ni-R	8	1.5109	.0098					Do.
45 Ni-R	9	1.5100	.0097					Do.
45 Ni-R	10	1.5096	.0097					Do.

[a] Ni-K is nickel on kieselguhr; Ni-R is Raney nickel.
[b] Values in parentheses were estimated.

The catalyst used in the first experiment on fraction *C–20* (wt about 14 g) was nickel-on-kieselguhr, prepared as described by Adkins [4]. The hydrogenation of acetone with this catalyst was found to proceed readily and at about the rate reported by Adkins. Naphthalene also was readily hydrogenated to decahydronaphthalene. Seven treatments using 3- and 10-g portions of catalyst were required before fraction *C–20* was free from nonnaphthenic material.

In the second experiment, with fraction *C–13*, the catalyst recovered from each treatment was tested for NiS, which was found up to the fourth treatment, with a trace in the fifth. A total of 10 g of nickel-on-kieselguhr and 52 g of Raney [5] nickel was used in this experiment.

In the next experiment with fraction *C–7*, which contained 1.5 percent of sulfur, 50 g of Raney nickel in the first treatment was sufficient to remove the sulfur completely. It is evident, at least during the first treatment of these oils with high sulfur content, that a large quantity of catalyst (50 g catalyst for 20 g of oil) is advantageous.

The experiment with fraction *E–1* is included in table 1 because in addition to its high sulfur content this oil contained 0.71 percent of nitrogen. The solution of oil in solvent smelled strongly of ammonia after each treatment from the second to the sixth, and a faint ammoniacal odor could be detected after the seventh treatment. It is probable that ammonia was present after the first treatment but was overlooked. This fraction was treated 10 times and in the final stages the hydrogenation progressed extremely slowly.

Since there seemed to be no advantage in the use of nickel-on-kieselguhr, Raney nickel was used in all experiments except the first and part of the second. One hydrogenation treatment was made with Raney nickel produced from the commercial alloy, as described by Adkins [4]. The results of this treatment were in no way superior to those obtained with the commercial catalyst preserved in water which was used in the remainder of the experiments. Solvent was necessary on account of the large ratio of catalyst to oil.

IV. HYDROGENATION PROCEDURE

The procedure finally adopted in the hydrogenation treatments was as follows: The oil fraction (12 to 30 g) was dissolved in 75 ml of methylcyclohexane and transferred to the liner. About 40 to 50 g of Raney nickel which was stored under water was transferred to a sintered glass filter and most of the water drawn off by suction. It was then washed with alcohol and finally with methylcyclohexane, and transferred while still wet to the liner, which was previously filled with carbon dioxide.

After each hydrogenation treatment of from 10 to 12 hours at 230° to 250° C, the oil and solvent were separated from the catalyst with the use of a sintered-glass filter, and the catalyst was washed with more methylcyclohexane. The refractive index and refractive dispersion were determined on a small portion of the oil from which the solvent had been removed by heating in vacuum. After removal by

[5] Raney nickel, a product developed by Murray Raney, was purchased from the Gilman Paint and Varnish Co., of Chattanooga, Tenn. This catalyst is prepared from a finely ground nickel-aluminum alloy by dissolving the aluminum with sodium hydroxide solution.

distillation of the extra solvent used in washing, the oil was ready for the next treatment with a fresh portion of catalyst. After the final treatment, the solvent was removed from the oil by distillation and finally by sweeping out at 110° C at a low pressure (25 mm) with carbon dioxide.

The loss of oil in a complete hydrogenation was usually from 2 to 4 g (about 10 to 20 percent), about 1 g of which could be accounted for as adhering to the walls of the vessel in which the sample was freed from solvent. The oil became water-white after the first treatment.

Hydrogenation treatments on any fraction were continued until the specific dispersion, $(n_F - n_C)/d \times 10^4$, decreased to about 100, a value (discussed later) characteristic of naphthenes.

V. DETERMINATION OF PHYSICAL PROPERTIES

The same methods were employed in determining the physical properties of the hydrogenated fractions as were employed in determining their properties before hydrogenation. These methods have been described elsewhere [3].

VI. DISCUSSION OF RESULTS

The physical properties of the fractions before and after hydrogenation are recorded in table 2. That there has been a fundamental change in most of the physical properties is obvious. Since a detailed discussion of these properties will be given in a subsequent paper, only the more obvious differences will be pointed out here.

TABLE 2.—*Physical properties of hydrogenated and unhydrogenated fractions*

Fraction	Percentage extracted	Number of treatments with hydrogen	Kinematic viscosity at—		Kinematic-viscosity index [c]	Refractive index [b] n_D^{25}	Density [c] at 25° C	Refractive dispersion $n_F - n_C$ at 25° C	Specific optical rotation $[\alpha]_D^{20}$	Aniline point	Specific refraction [d] $\frac{n^2-1}{n^2+2}\times\frac{1}{d}$	Specific dispersion [d] $\frac{n_F-n_C}{d}$
			100° F	210° F								
			Stokes	*Stokes*			*g/ml*			°C		
B-12	33.7 to 36.4		12.0	0.150	−560	1.5952	1.030	0.0236			0.3299	0.0229
B-12-H		4	1.37	.0740	−143	1.5000	0.9291	.0093		84.0	.3166	.0100
B-16	44.5 to 47.2		8.31	.144	−369	1.5785	1.010	.0207	(0.42)	−3.5	.3287	.0205
B-16-H		5	1.49	.0791	−124	1.5000	0.9272	.0093	.19	85.8	.3173	.0100
B-19	52.4 to 54.8		5.60	.130	−269	1.5052	.9942	.0187	(.57)	(6.9)	.3277	.0188
B-19-H		4	1.42	.0809	−91	1.4991	.9244	.0093	.30	87.8	.3177	.0101
C-1 [a]	0 to 5.2		(300)*	.340	(−3,500)*	(1.641)	1.076	(.032)	(.05)*		.3353	(.030)*
C-1-H		8	2.79	.0907	−284	1.5044	0.9381	.0094	.03	82.4	.3159	.0100
C-7	20.6 to 23.9		70.3	.253	−1,340	1.6189	(1.05)	(.0281)	(.27)		(.333)	(.0267)
C-7-H		5	3.67	.107	−254	1.5059	0.9417	.0093	.15	82.4	.3154	.0099
C-13	37.3 to 39.9		29.8	.229	−606	1.5911	1.025	.0234	(.50)		.3298	.0228
C-13-H		5	4.16	.121	−199	1.5047	0.9389	.0092	.19	84.9	.3157	.0098
C-20	55.0 to 57.2		9.87	.182	−223	1.5622	.9909	(.0183)	(.83)	14.4	.3274	(.0185)
C-20-H		7	2.70	.112	−96	1.5005	.9280	.0092	.31	90.6	.3172	.0099
C-(26+27)	66.7 to 70.3		(2.95)	(.125)	(−61)	(1.5325)	(.956)	(.0140)	(1.14)	(35.7)	(.3245)	(.0147)
C-(26+27)-H		5	1.78	.102	−27	1.4947	.9136	.0090	0.48	96.9	.3190	.0099
C-30	74.1 to 75.9		1.72	.103	−14	1.5215	.9403	.0125	(.89)	44.2	.3241	.0133
C-30-H		2	1.30	.0912	+1	1.4909	.9047	.0090	.42	98.9	.3201	.0099
C-33	80.3 to 82.5		1.01	.0806	+8	1.5111	.9230	.0117	(.59)	(50.6)	.3246	.0127
C-33-H		2	0.898	.0809	+37	1.4868	.8944	.0089	.28	101.2	.3215	.0100
C-35	84.5 to 86.7		.738	.0752	+53	1.5056	.9124	.0112	(.41)	55.9	.3254	.0123
C-35-H		2	.687	.0718	+51	1.4823	.8837	.0088	.19	104.0	.3228	.0100
C-37	88.9 to 91.2		.570	.0674	+69	1.4993	.8996	.0106	.38	62.4	.3266	.0118
C-37-H		1	.586	.0691	+72	1.4799	.8755	.0087	.38	105.4	.3244	.0099
C-res	96.3 to 100		.364	.0579	+112	1.4711	.8560	.0082	.81	111.1	.3266	.0096
C-res.-H		1	.365	.0571	+107	1.4707	.8552	.0084	.82	112.3	.3267	.0098
E-1 [a]	0 to 8.8		(>1,000)*	(>1.8)*	(<−2,000)*	(1.63)*	1.074	(.030)*			(.334)*	(.028)*
E-1-H		10	48.8	.282	−671	1.5096	0.9466	.0097		90.4	.3158	.0102
E-25	72.6 to 75.3		4.51	.187	+10	1.5210	(.943)	(.0124)	(.92)	(57.3)	(.3238)	(.0132)
E-25-H		4	3.11	.156	+19	1.4920	.9047	.0092		109.1	.3207	.0102

Fraction	Boiling point at 1mm Hg	Molecular weight	Combustion analyses: Ratio moles H_2O/CO_2	Combustion analyses: Mass of sample less mass of C+H	Sulfur content	Nitrogen content	Oxygen content	In the formula $C_nH_{2n+z}S_yN_xO_w$: n	x	y	z	w
	°C			*Percent by wt*	*Percent by wt*	*Percent by wt*	*Percent by wt*					
B-12	(202)	(308)	(0.604)	(2.36)				(22.7)	(−18.00)			
B-12-H	169	314	.8747	0.06				22.8	−5.71			
B 16	(202)	(318)	(.656)	(1.78)				(23.4)	(−16.10)			
B-16-H	176	324	.8777	0.07				23.5	−5.74			
B-19	(202)	(326)	(.682)	(1.26)				(24.1)	(−15.35)			
B-19-H	179	329	.8827	0.08				23.9	−5.60			
C-1 [a]	218	303	.5363	2.63	0.77	0.56	1.30	22.5	−20.90	0.07	0.12	0.25
C-1-H	168	309	.8676	0.08				22.5	−5.95	.0	.0	.0
C-7	(217)	(318)	(.581)	(2.38)	(1.53)	(.05)	(0.80)	(23.5)	(−19.70)	(.15)	(.01)	(.16)
C-7-H	179	329	.8655	0.16				23.5	−6.33	.0	.0	.0
C-13	(217)	(330)	(.637)	(2.12)	(1.40)	(.02)	(.70)	(24.4)	(−17.72)	(.14)	(.00)	(.14)
C-13-H	188	341	.8686	0.16				24.7	−6.49	.0	.0	.0
C-20	(217)	(347)	(.696)	(1.45)	(0.90)	(.01)	(.53)	(25.5)	(−15.50)	(.10)	(.00)	(.11)
C-20-H	197	353	.8807	0.03				25.6	−6.11	.0	.0	.0
C-(26K27)	(216)	(372)	(.759)	(1.0)	(.50)	(.01)	(.49)	(27.2)	(−13.10)	(.03)	(.00)	(.11)
C-(26K27)-H	204	376	.8977	0.04				27.2	−5.57	.0	.0	.0
C-30	(215)	(384)	(.794)	(.73)	(.36)	(.01)	(.36)	(28.0)	(−11.55)	(.04)	(.00)	(.09)
C-30-H	208	384	.9086	.04				27.7	−5.07	.0	.0	.0
C-33	(215)	(390)	(.814)	(.64)	(.34)	(.00)	(.30)	(28.4)	(−10.56)	(.04)	(.00)	(.07)
C-33-H	210	393	.9215	.02				28.3	−4.45	.0	.0	.0
C-35	(216)	(393)	(.829)	(.70)	(.36)	(.00)	(.34)	(28.5)	(−9.75)	(.04)	(.00)	(.08)
C-35-H	212	396	.9314	.08				28.5	−3.91	.0	.0	.0
C-37	(216)	(401)	(.852)	(.60)	(.30)	(.00)	(.30)	(29.0)	(−8.6)	(.04)	(.00)	(.07)
C-37-H	216	402	.9436	.03				28.9	−3.26	.0	.0	.0

See footnotes at end of table.

TABLE 2.—*Physical properties of hydrogenated and unhydrogenated fractions*—Continued

Fraction	Boiling point at 1 mm Hg	Molecular weight	Combustion analyses		Sulfur content	Nitrogen content	Oxygen content	In the formula $C_nH_{2n+z}S_yN_xO_w$				
			Ratio moles H_2O/CO_2	Mass of sample less mass of C+H				n	z	y	z	w
	° C			*Percent by wt*	*Percent by wt*	*Percent by wt*	*Percent by wt*					
C-res	219	420	.9696	.02				30.1	−1.85	(.00)	(.00)	(.00)
C-res.-H	220	417	.9716	.04				29.9	−1.69	.0	.0	.0
E-1 [a]	(256)	367	.5666	2.98	.81	.71	1.46	27.1	−23.46	.09	.19	.33
E-1-H	207	367	.8639	0.06				26.7	−7.26	.0	.0	.0
E-25	(256)	(456)		(.6)	(.34)	(.01)	(.25)	33.1	(−11.7)	(.05)	(.00)	(.07)
E-25-H	247	455	.9141	.06				32.8	−5.64	.0	.0	.0

[a] Values in parentheses were estimated by interpolation or extrapolation. Those with an asterisk (*) are rough estimates.

[b] The values of the refractive index may be converted to other temperatures by using for dn_D/dt the value 0.00038 per ° C. Over a 5-degree temperature interval, this conversion will not introduce an uncertainty greater than ±0.0002.

[c] The values of the density may be converted to other temperatures by using for dD/dt the value 0.0007 g/ml per ° C. Over a 5-degree interval, this conversion will not introduce an uncertainty greater than ±0.0003 g/ml.

[d] The values for the specific refraction and specific dispersion may be regarded as constant over a 5-degree range of temperature within the accuracy of these measurements.

[e] Kinematic-viscosity indices were computed with the aid of the tables given by Hersh, Fisher, and Fenske [5].

The change in physical properties on hydrogenation is very pronounced for the first fraction extracted, and is almost negligible for the residue. For the first fractions extracted, there is on hydrogenation a great decrease in viscosity and a marked increase in viscosity index. The refractive index, density, refractive dispersion, specific refractive dispersion, specific optical rotation, and specific refraction decrease pronouncedly. The aniline point increases and the boiling point decreases. There is a slight increase in molecular weight. The number of carbon atoms per molecule, however, remains constant. The results of the combustion analyses show, of course, an increase in the ratio of hydrogen to carbon. They show also that the sulfur, nitrogen, and oxygen (except for a trace) have been removed by the hydrogenation process.

For the purpose for which the data on the hydrogenated fractions are to be employed, it is important to know that there has been no loss of carbon atoms in the hydrogenation process and that after hydrogenation the fractions are substantially free from nonnaphthenic material.

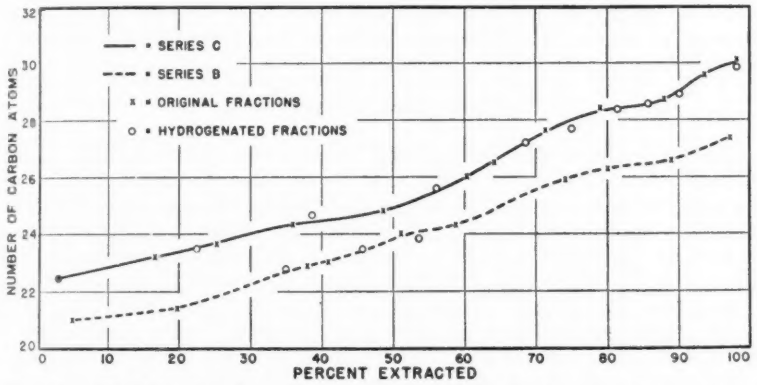

FIGURE 2.—*Number of carbon atoms per molecule for the fractions from extractors B and C, before and after hydrogenation.*

1. MOLECULAR WEIGHT

In figure 2 the number of carbon atoms per molecule, both for the original fractions from two series (*B* and *C*) and for the fractions after hydrogenation, is plotted with respect to the percentage extracted. It is apparent that the points fall close to smooth curves, and that the number of carbon atoms per molecule for the hydrogenated fractions, as estimated from the curves, does not differ by more than about 0.2 carbon atom from that experimentally determined. This is within the limits of accuracy of the molecular-weight determinations, and it may be concluded that there has been no loss of carbon atoms in the hydrogenation process.

From a consideration of the specific refractive dispersions, specific refractions, and the behavior of the fractions on treatment with silica gel, it is possible to ascertain whether these fractions are substantially free from aromatic hydrocarbons.

2. SPECIFIC REFRACTIVE DISPERSION

Vlugter, Waterman, and Van Westen [6] have pointed out that an oil is practically free from aromatic hydrocarbons when the specific dispersion, $(n_G-n_C)/d\times10^4$, is less than 158. Von Fuchs and Anderson [7] found, in a review of dispersion data for synthetic hydrocarbons, principally those of low molecular weight, that the values for the specific dispersion, $(n_F-n_C)/d\times10^4$, of naphthenes and paraffins lie in the region 95 to 102—the average value for the naphthenes being 98.3 and that for paraffins 98.4. Five of the six 1- and 2-ring naphthene hydrocarbons of high molecular weight synthesized by Mikeska [7] have specific dispersions, $(n_F-n_C)/d\times10^4$, between 97 and 100, and confirm the observation of Von Fuchs and Anderson [7]. It is apparent that if fractions have specific dispersions $\times10^4$ of 100 or less they contain little, if any, aromatic hydrocarbons.

Of the 15 fractions hydrogenated, 12 have specific refractions of 100 or less. For the two fractions *E–1* and *E–25*, specific dispersions of 102 were obtained. On the last hydrogenation treatment of *E–1*, the refractive index changed by only four units in the fourth decimal place, and the specific dispersion remained constant. For fraction *E–25* no change in either the refractive index or the refractive dispersion resulted from the final hydrogenation.

3. SPECIFIC REFRACTION

Figure 3 shows for comparison the values of the Lorentz-Lorenz specific refraction $(n^2-1)/(n^2+2)\times1/d$ of the hydrogenated fractions, together with two sets of theoretical curves of the specific refraction of paraffins and of 1-, 2-, 3-, and 4-ring naphthenes. The theoretical curves on the left are similar to those of Vlugter, Waterman, and Van Westen [1], and are based on the atomic refractions given by Eisenlohr for carbon (2.418) and for hydrogen (1.100). The theoretical curves on the right are based on the values of the atomic refractions of carbon (2.59) and hydrogen (1.025) obtained by van der Hulst [9] in a recent recalculation of the atomic refractions. The values in circles are x values in the expression C_nH_{2n+x} obtained for the hydrogenated fractions. The values in squares are the x values of fractions of "water-white" oil obtained by extraction and described elsewhere [10]. Only those fractions of water-white oil whose specific dispersions, $(n_F-n_C)/d\times10^4$, were 100 or lower have been plotted.

It is evident that there is a very considerable difference in the position of the two sets of theoretical curves, and that the values for the specific refractions of the oil fractions are all much too low to correspond with the curves based on van der Hulst's values. The specific refractions of most of the water-white oil fractions are in good agreement with the curves based on Eisenlohr's values. The specific refractions of the hydrogenated fractions are a little too high and lie between the two sets of curves. Waterman and Leendertse [11] also have found that the specific refractions of a series of oils prepared by complete hydrogenation of mineral oils and of polymerized olefins were much too low to agree with van der Hulst's values and a little too high to agree with Eisenlohr's values. Since both our values and those of Waterman and Leendertse are in much better agreement with Eisenlohr's values, and since refraction values higher but not

FIGURE 3.—*Specific refractions of hydrogenated and of water-white oil fractions compared with theoretical curves for the specific refractions.*

The curves at the left are based on Eisenlohr's atomic refractions; those on the right are based on van der Hulst's atomic refractions.

lower than the theoretical curves might be accounted for as due to the presence of small amounts of aromatics or unsaturated hydrocarbons, Eisenlohr's values seem preferable.

It should be pointed out that these curves are based on the atomic refractions of carbon and hydrogen obtained from aliphatic compounds, and that no allowance is made for ring formation or for the various types of rings which may be present and which may influence to a minor extent the specific refraction. Consequently, although gross deviations from these curves are undoubtedly due to nonnaphthenic material, small deviations may or may not signify the presence of traces of aromatic or unsaturated material.

4. SILICA GEL EXPERIMENTS

To test further whether aromatic or unsaturated hydrocarbons were present in small amounts, two of these fractions, *E–1* and *C–26+27*, of about 15 g each, were mixed with two volumes of pure methylcyclohexane and filtered through a 30-cm column containing 5 g of fine silica gel.[6] Some of the physical properties were again determined and are recorded in table 3. A very small change in physical properties occurred; the refractive index and density decreased, the hydrogen content increased, and the molecular weight increased. The change in the x value for fraction *C–26+27* was insignificant, while for fraction *E–1* it changed only from −7.26 to −7.40. This treatment also showed no evidence of any significant quantity of aromatic hydrocarbons, and the small change in properties which occurred may be attributed to a fractionation on the basis of molecular weight. The agreement between the specific refraction of the samples after treatment and the theoretical curves, based on Eisenlohr's atomic refractions, was scarcely improved.

[6] Silica gel has been found to remove completely aromatic and unsaturated hydrocarbons from naphthenes or paraffins in the gasoline region [12] and also, where tested, in the lubricating oil region [13].

TABLE 3.—*Physical properties of hydrogenated fractions before and after silica gel treatment*

TABLE 3.—*Physical properties of hydrogenated fractions before and after silica gel treatment*

Fraction		Refractive index n_D^{25}	Refractive dispersion $n_F - n_C$ at 25° C	Density at 25° C	Specific refractive dispersion $\frac{n_F - n_C}{d}$	Specific refraction $\frac{n_1 - 1}{n_1 + 2} \times \frac{1}{d}$	Molecular weight	Combustion analyses		In the formula C_nH_{2n+x}	
								Ratio: moles H_2O/CO_2	Mass of sample less mass of C+H	n	x
				g/ml					*Percent by wt.*		
C-26+27	Before	1.4947	0.0090	0.9135	0.0099	0.3190	376	0.8977	0.04	27.2	−5.57
	After	1.4936	.0090	.9128	.0099	.3187	386	.9009	.05	27.9	−5.53
E-1	Before	1.5096	.0097	.9466	.0102	.3158	367	.8639	.06	26.7	−7.26
	After	1.5082	.0097	.9461	.0103	.3151	378	.8653	.06	27.5	−7.40

5. ANILINE POINT

Since Vlugter, Waterman, and Van Westen [1] give a series of curves showing the relationship between aniline points and specific refractions for hydrogenated fractions of different molecular weights, a comparison is possible between the aniline points found by them and those found in this investigation. In table 4 are compared the aniline points of fractions with the same molecular weight and specific refraction. In some instances, the values found in this investigation are higher and in some instances lower than those found by Vlugter, Waterman, and Van Westen, but considering the fact that the comparison involves not only the determination of aniline points but also of molecular weight, refractive index, and density, the agreement is good.

TABLE 4.—*Aniline points of hydrogenated fractions compared with those of Vlugter, Waterman, and Van Westen*

Fraction	Aniline points		Fraction	Aniline points	
	This work	Vlugter, Waterman, and Van Westen		This work	Vlugter, Waterman, and Van Westen
B-12-*H*	84.0	83	*C*-30-*H*	98.9	98
B-16-*H*	85.8	86	*C*-33-*H*	101.2	101
B-19-*H*	87.8	87			
C-1-*H*	82.4	81.5	*C*-35-*H*	104.0	103.7
C-7-*H*	82.4	84.0	*C*-37-*H*	105.4	107.0
			C-res-*H*	112.3	112.0
C-13-*H*	84.9	85.5	*E*-1-*H*	90.4	90
C-20-*H*	90.6	90.0	*E*-25-*H*	109.1	112
C-26-27-*H*	96.9	95.5			

VII. CONCLUSION

The data on these completely hydrogenated fractions will be utilized in a subsequent paper to give information as to the chemical composition of the extract portion of the petroleum from which they were derived.

The authors express their gratitude for the advice and encouragement of F. D. Rossini.

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CHEMICAL CONSTITUTION OF THE "EXTRACT" PORTION OF THE LUBRICANT FRACTION FROM A MIDCONTINENT PETROLEUM[1] *

By Beveridge J. Mair, Charles B. Willingham, and Anton J. Streiff[2]

ABSTRACT

A correlation has been made of the properties of 179 fractions of oil prepared by extensive distillation and extraction of the extract portion of the lubricant fraction from a midcontinent petroleum. The correlation includes a comparison of the properties of these fractions with those of a selected 15 of the same fractions after complete hydrogenation, with those of synthetic hydrocarbons of high molecular weight, and with those of fractions of "water-white" oil previously prepared from this same lubricant fraction.

The following physical and chemical properties have been compared: Specific optical dispersion, specific optical refraction, specific optical rotation, aniline point, viscosity at 100° and at 210° F, kinematic-viscosity index, and boiling point at 1 mm Hg. The sulfur, oxygen, and nitrogen content and the value of x in the expression C_nH_{2n+x} have also been considered.

Concerning the chemical constitution of the lubricant fraction of a midcontinent petroleum from which the "wax" and "asphaltic" constituents have been removed, the following conclusions are drawn: (1) about 60 percent of the material consists of naphthenes with from 1 to 3 rings per molecule (a very small amount of material containing 4 naphthenic rings is probably present also); (2) about 15 percent of the material consists of molecules with 1 aromatic ring and from 1 to 3 naphthenic rings per molecule, together with a small amount of sulfur and oxygen compounds; (3) about 14 percent of the material consists of molecules with 2 aromatic rings (linked through two common carbon atoms) and about 2 naphthenic rings per molecule, together with a small amount of sulfur and oxygen compounds; (4) about 11 percent of the material consists of molecules with more than 2 aromatic rings (each probably linked through two common carbon atoms) and 1 or 2 naphthenic rings per molecule, together with some sulfur, nitrogen, and oxygen compounds.

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[2] Research Associates at the National Bureau of Standards, representing the American Petroleum Institute.

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I. INTRODUCTION

Two years ago this laboratory prepared several series of fractions of water-white oil by extensive distillation and extraction of the lubricant fraction from a midcontinent petroleum. Certain physical properties of these fractions were determined and conclusions were drawn as to the chemical nature of the fractions [1, 2,].[3] To obtain a more complete picture of the constitution of the lubricant fraction five series of fractions were prepared in an analogous manner from the extract portion of the same oil and a number of their physical properties determined [3]. Fifteen of these fractions were completely hydrogenated to naphthenes and their physical properties again determined [4]. In this paper data on the extract fractions, the hydrogenated fractions, and the water-white oil are correlated with data available in the literature on synthetic hydrocarbons. Although special consideration is given to the chemical composition of the extract portion, conclusions are drawn as to the constitution of the entire lubricant fraction, except for wax and asphaltic constituents.

II. ORIGIN OF THE PETROLEUM FRACTIONS AND SOURCES OF THE DATA USED IN THIS CORRELATION

The lubricating-oil stock came from well No. 6 of the South Ponca Field, Kay County, Okla. The lubricant fraction was distilled in vacuo by the Sun Oil Co., Philadelphia, Pa., before receipt at this Bureau. Its treatment in this laboratory is illustrated diagrammatically in figure 1. It consisted in (1) the separation of an extract portion by extraction with liquid sulfur dioxide at room temperature, (2) the separation of a wax portion by crystallization from ethylene chloride at −18° C, and (3) the separation of the remainder by filtration through silica gel into two portions (a) a water-white portion, and (b) a portion recovered from silica gel and listed in figure 1 as silica gel "hold-up." As shown in figure 1, the extract portion was further separated, by extraction with sulfur dioxide and petroleum ether at −55° C, into two portions, one of which, denoted as "asphaltic material", was placed in storage. The petroleum ether-soluble portion was mixed with the silica gel hold-up and the mixture systematically distilled. Five charges, denoted as *A*, *B*, *C*, *D*, and *E*, were prepared from the distillation fractions and each charge was separated into a series of 30 to 40 fractions by extraction with methyl cyanide in 16.7-m (55-ft) columns. The properties of these fractions have been compared with each other and with the properties of 3 fractions from series *B*, with 10 from series *C*, and with 2 from series *E*, after their complete hydrogenation [4]. They have also been compared with the properties of several series of water-white oil fractions previously prepared by distillation and extraction from the same lubricant fraction [1].

The data used for comparison come, for the extract fractions, from tables 9 and 10 of reference [3]; for the hydrogenated fractions, from table 4 of reference [4]; and for the water-white oil fractions, from tables 2 and 3 of reference [1].

[3] Figures in brackets indicate the literature references at the end of this paper.

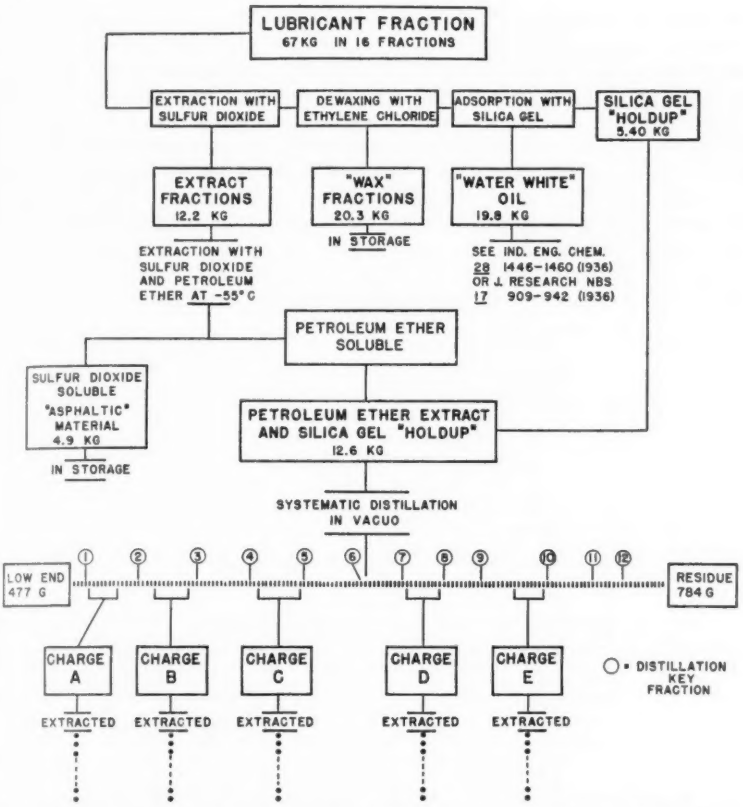
LUBRICANT FRACTION
67 KG IN 16 FRACTIONS
EXTRACTION WITH SULFUR DIOXIDE
DEWAXING WITH ETHYLENE CHLORIDE
ADSORPTION WITH SILICA GEL
SILICA GEL "HOLDUP" 5.40 KG
EXTRACT FRACTIONS 12.2 KG
"WAX" FRACTIONS 20.3 KG
IN STORAGE
"WATER WHITE" OIL 19.8 KG
EXTRACTION WITH SULFUR DIOXIDE AND PETROLEUM ETHER AT −55° C
SEE IND. ENG. CHEM. 28 1446–1460 (1936) OR J. RESEARCH NBS 17 909–942 (1936)
PETROLEUM ETHER SOLUBLE
SULFUR DIOXIDE SOLUBLE "ASPHALTIC" MATERIAL 4.9 KG
IN STORAGE
PETROLEUM ETHER EXTRACT AND SILICA GEL "HOLDUP" 12.6 KG
SYSTEMATIC DISTILLATION IN VACUO
LOW END 477 G
1 2 3 4 5 6 7 8 9 10 11 12
RESIDUE 784 G
CHARGE A
CHARGE B
CHARGE C
CHARGE D
CHARGE E
EXTRACTED
EXTRACTED
EXTRACTED
EXTRACTED
EXTRACTED
○ • DISTILLATION KEY FRACTION

FIGURE 1.—*Chart showing treatment and disposition of lubricating oil fractions.*

III. DISCUSSION OF PHYSICAL PROPERTIES AND CHEMICAL CONSTITUTION

1. SPECIFIC REFRACTIVE DISPERSION [4]

It is evident from figure 2 that there is a general similarity in the shape of these curves for the specific dispersion and that pronounced changes in slope occur at approximately the same percentage extracted. Curves for series *A* and *E*, though not unlike those of *B*, *C*, and *D*, are not included since their presence would mechanically complicate the figure.

Both Vlugter, Waterman, and Van Westen [5] and Von Fuchs and Anderson [6] have used specific dispersion as a means of obtaining information concerning the chemical constitution of petroleum fractions. The former have used the *G* and *C* lines, and have pointed out that an oil is practically free from aromatic hydrocarbons when $(n_G - n_C)/d$ is less than 158×10^{-4}. In Von Fuchs and Anderson's [6] recent review of specific dispersion values of synthetic hydrocarbons,

[4] For convenience values of the specific dispersion given in the text refer to values of $\frac{n_F - n_C}{d} \times 10^4$.

principally those of low molecular weight, the values of the specific dispersion are in the region 95 to 102 for naphthenes and paraffins and the average value for all the paraffins is 98.4 and for all the naphthenes 98.3. Von Fuchs and Anderson point out that these values are practically independent of molecular weight. Five of six 1- and 2-ring naphthenes of high molecular weight synthesized by Mikeska [7] have values for the specific dispersion between 97 and 100 and confirm the observation of Von Fuchs and Anderson. Thirteen of the fifteen fractions prepared by hydrogenation in this investigation [4] had specific dispersion values of 100 or lower. Consequently, the straight line drawn at 98.4 in figure 3 represents approximately the specific dispersion values for naphthenes and paraffins.

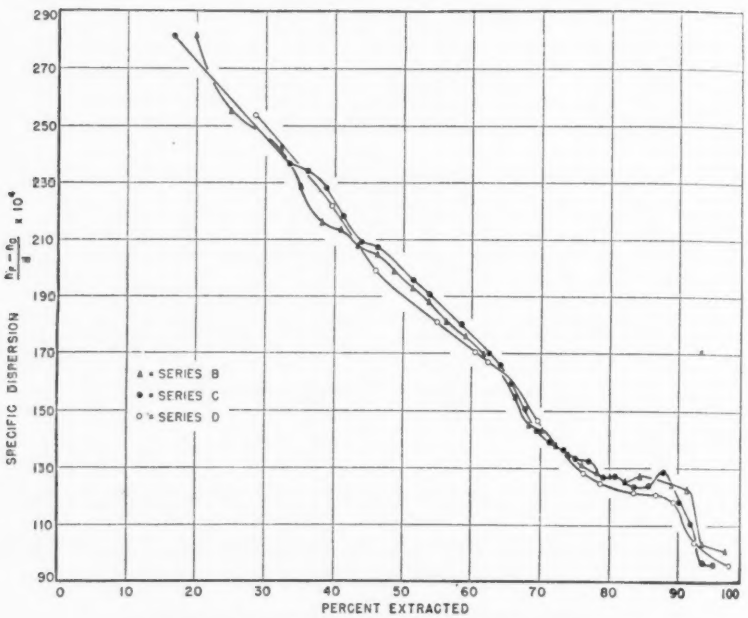

FIGURE 2.—*Specific dispersion of petroleum fractions.*

In figure 2 and in all subsequent figures in which a property is plotted with respect to the percentage extracted, the average value for the percentage extracted has been used. Thus fraction *C-5* which was the extract obtained between 15.3 and 17.9 percent of the charge, is represented by a point at 16.6 percent.

Von Fuchs and Anderson also give values for the specific dispersion of benzene and some of its homologues and point out that the dispersion decreases as the number of nonbenzenoid carbon atoms increases. Mikeska [7] gives values for several compounds of this type of high molecular weight. Curve *III*, figure 3, is drawn through the values recorded by Von Fuchs and Anderson for benzene and its homologues of low molecular weight and through those benzene and tetralin homologues of high molecular weight given by Mikeska. Similarly, curve *I* is drawn through the specific dispersions given by Von Fuchs and Anderson for naphthalene and its homologues of low molecular weight, and through the values given by Mikeska for those of high molecular weight. As Von Fuchs and Anderson point out,

the specific dispersion of naphthalene and its homologues in which the aromatic rings have two carbon atoms in common are abnormally high when compared with hydrocarbons in which the rings are connected through a nonbenzenoid carbon atom. Curve *II* is drawn for 2-ring aromatic hydrocarbons in which the connection between rings is through nonbenzenoid carbon atoms. This curve is based on values for two hydrocarbons of low molecular weight reported by Von Fuchs and Anderson, and on the value 142 for 1,1-diphenylhexadecane and 143 for 1-phenyl-2-benzylheptadecane, synthesized by Landa and

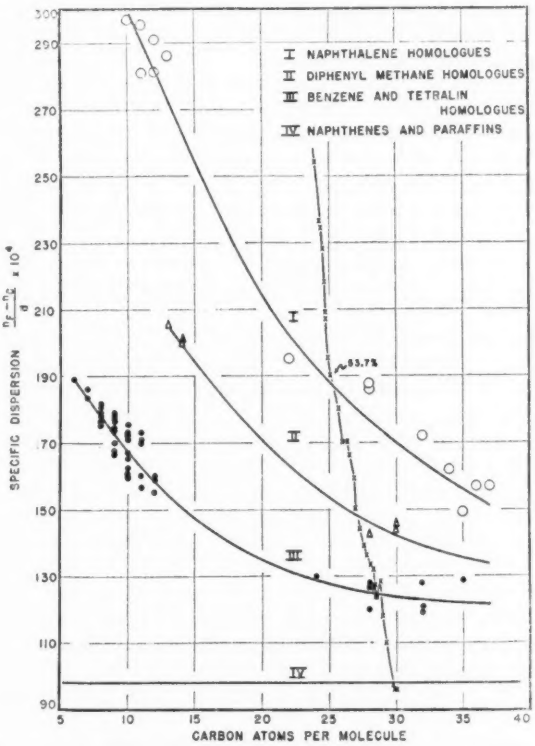

FIGURE 3.—*Specific dispersion of synthetic hydrocarbons with respect to the carbon atoms per molecule.*

Cech [8]. A point is also plotted for 1,1-diphenyloctadecane synthesized by Mikeska [7], although other properties reported for this compound are not what would be expected. Hydrocarbons with 2 aromatic rings directly connected at one point will have values lying between curves *I* and *II*. Included in this figure is a line showing the specific dispersions of the fractions from extractor *C*. On this line is indicated one point which represents the fraction extracted at 53.7 percent. Evidence is given later to show that this fraction contains essentially compounds with 2 aromatic rings, with the rings linked through two common carbon atoms, and this is in agreement with its specific dispersion.

An interpretation of the specific dispersions of the extraction fractions may be obtained by comparing figures 2 and 3. Here and later in this paper it is convenient in the interpretation of these figures to begin at the right-hand side of the figures and consider the curves in the direction of decreasing percentages extracted. In figure 2, each curve shows a nearly horizontal portion in the region from about 100 to 94 percent extracted. In this region the specific dispersions vary from 96 to 101, and it is evident that they contain little, if any, aromatic material. Since paraffins are probably absent because the value for x in the expression C_nH_{2n+x}, is negative these fractions are composed principally of naphthenes. Each curve shows another relatively flat portion at from 92 to 76 percent, the specific dispersions here varying from about 122 to 130. These values are in good agreement with the values for homologues of benzene with the same number of carbon atoms (i. e., 28 to 32), and indicate that the fractions are composed chiefly of molecules containing 1 aromatic ring and the necessary aliphatic side chains and naphthenic rings.

Considering now the region from 76 to 62 percent, and in particular series *C*, there is a slow increase in specific dispersion from 132 at 76 percent to 140 at 71 percent, and from there a more rapid increase to 175 at 62 percent, after which the dispersion again increases somewhat more slowly. These changes in slope are not very pronounced. They are called to attention, however, since changes in other physical properties occur at or near these percentages. The rapid increase in dispersion from 140 at 71 percent to 175 at about 62 percent is presumably due to the transition from material composed substantially of 1-ring aromatic hydrocarbons to material composed largely of 2-ring aromatic hydrocarbons. As will be shown later, when comparing the hydrogenated with the unhydrogenated fractions, the specific dispersions in the region from 62 to 45 percent can be accounted for only on the supposition that the aromatic rings are directly joined through two common carbon atoms. The high specific dispersions (above 210) from about 42 to 18 percent can be accounted for by the presence of compounds containing more than 2 aromatic rings per molecule. The curves (except for series *B* which shows a break between 46 and 38 percent) show no pronounced changes in slope, and indicate that the transition from material with 2 aromatic rings per molecule to that containing 3 aromatic rings per molecule has not been sharp.

2. SPECIFIC REFRACTION

The curves in figure 4, like those for the specific dispersion, show a general similarity in shape, but, unlike those for the specific dispersion, they show several pronounced maxima and minima. An interpretation of the values for the refraction and the maxima and minima shown by these curves may be obtained by comparing figures 4 and 5.

Vlugter, Waterman, and Van Westen [11] have shown that the Lorentz-Lorenz specific refractions may be used for determining the number of rings in aromatic-free oils, and conversely, for determining whether an oil is aromatic-free by comparing its x value obtained from the carbon-hydrogen ratio and molecular weight with that obtained

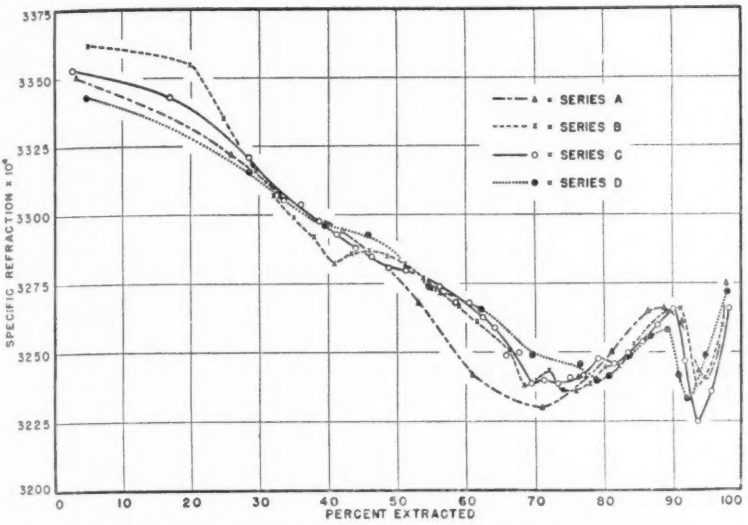

FIGURE 4.—*Specific refraction (Lorentz-Lorenz) of petroleum fractions.*

from its specific refraction. This latter method was used in this laboratory with the water-white oil [2] and the hydrogenated fractions prepared from the series under discussion [4]. In figure 5

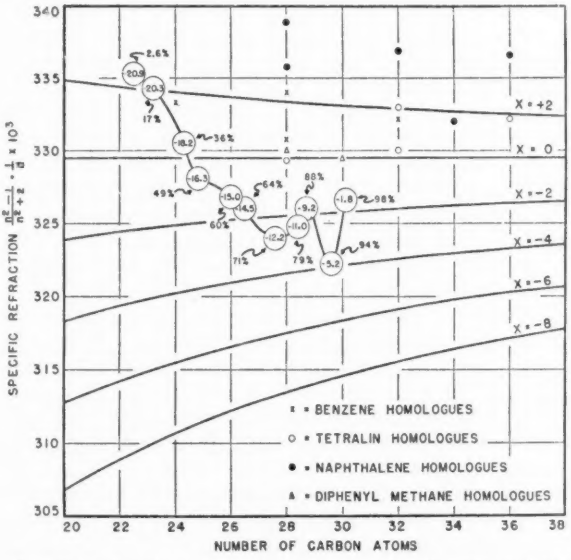

FIGURE 5.—*Specific refraction of fractions from series C compared with theoretical curves for naphthenes and paraffins and with synthetic aromatic hydrocarbons.*

theoretical curves, similar to those of Vlugter, Waterman, and Van Westen [11], show the variation in specific refraction with the number of carbon atoms for paraffins and for naphthenes containing 1, 2, 3, and 4 rings. Values for aromatic hydrocarbons, principally those

of Mikeska [7], are included in this figure.[5] Also plotted in this figure are values for the specific refraction of the fractions from series *C*. Values for x in the expression C_nH_{2n+x} for these fractions are given in the large circles. The percentages represented by the fractions are also given.

Comparing figures 4 and 5, it is evident that the x value (−1.8) obtained for the residue from series *C*, represented by the point at 98.2 percent, is in good agreement with the x value obtained from the specific refraction, and confirms the conclusion drawn from the dispersion data, that this fraction consists of naphthenes. The fraction represented by 93.6 percent in figure 4, although it has a low specific dispersion, apparently contains a small amount of aromatic hydrocarbons since its x value (−5.2) differs considerably from that obtained from the specific refraction (—3.9). From 93.6 to about 90 percent there is a sharp increase in the refraction to a value of 0.3265, and for this fraction the specific dispersion is 128, which indicates that it consists principally of 1-ring aromatic hydrocarbons. However, the specific refraction has not risen to the value which would be expected by a comparsion with the synthetic hydrocarbons containing 1 aromatic ring. Furthermore, the specific refraction begins to decrease at 90 percent and attains a low value of 0.3239 in the region from 73 to 69 percent, although the specific dispersion remains fairly constant between 90 and 76 percent and increases only slightly at 71 percent.

The relatively low value for the specific refraction, and its decrease to a minimum at 73 to 69 percent, can be accounted for on the supposition that in addition to 1 aromatic ring these molecules contain naphthenic rings, and that the average number of naphthenic rings per molecule increases from 90 to 69 percent extracted. This supposition will be confirmed later when considering the hydrogenated fractions. The sharp increase in specific refraction beginning at about 69 percent indicates a transition to material containing 2 aromatic rings per molecule. Another maximum at 46 percent and a minimum at 41 percent occur for series *B*, and correspond approximately with the breaks in specific dispersion occurring between 46 and 38 percent for the same series. It is possible that this minimum corresponds roughly with the end of the 2-ring aromatics.

The question may be asked why changes in slope of the specific dispersion and specific refraction curves do not occur at precisely the same percentages extracted for any one series. Why, for example, does the specific dispersion begin to increase slowly for series *C* at 77 percent, while the specific refraction continues to decrease to 69 percent? Specific dispersion is a property which is extremely sensitive to changes in the number of aromatic rings but is practically uninfluenced by the number of naphthenic rings. On the other hand, specific refraction is sensitive to the number of naphthenic rings but not as sensitive to the presence of aromatic rings as specific dispersion. For this reason simultaneous analysis of the refraction and dispersion curves serves to yield the maximum amount of information from the data on refraction and dispersion. In the region from 77 to 69 percent there is, as will be shown later, a slight increase in the average

[5] Compound 48 of Mikeska [7], i. e., 1,1-diphenyloctadecane was not included because most of the physical properties of this compound are out of line. Values for two compounds synthesized by Landa and Cech [8], 1,1-diphenylhexadecane and 1-phenyl-2-benzylhexadecane, are included, however.

number of aromatic rings per molecule; that is, a few percent of 2-ring aromatic hydrocarbons are present, which causes the increase in specific dispersion, but the number of naphthenic rings are increasing at such a rate that their influence predominates (as far as the specific refraction is concerned) and causes the specific refraction to decrease to 69 percent.

In figure 6 the simpler Gladstone-Dale expression $(n-1)/d$ is used. There is also plotted in this figure the "refractivity intercept," $n-d/2$, a quantity which has been proposed by Kurtz and Headington [9] and Kurtz and Ward [10] for use in analyzing hydrocarbon mixtures. The similarity of these two curves is obvious, and for these quantities also, as with the Lorentz-Lorenz specific refraction, there is a minimum in the neighborhood of 93.6 percent, though the depth of the minimum is not as great. Between 90 and 70 percent, instead of the

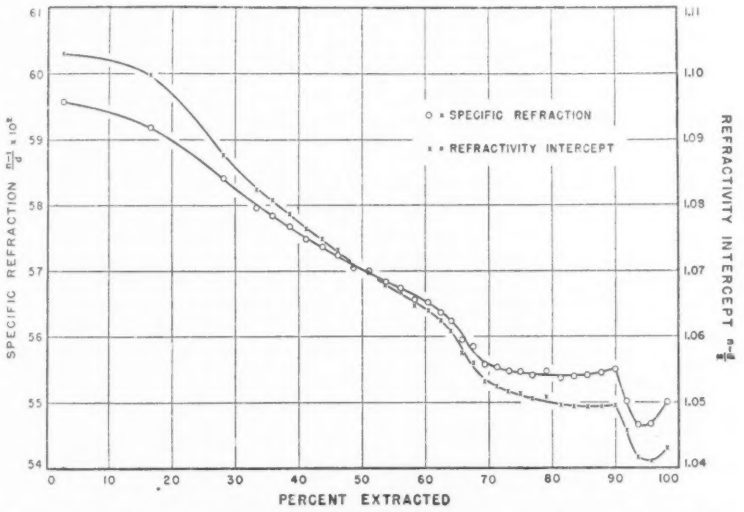

FIGURE 6.—*Specific refraction (Gladstone-Dale) and refractivity intercept of fractions from Series C.*

very pronounced minimum given by the Lorentz-Lorenz refraction, these curves are more nearly horizontal and indeed begin to rise in the neighborhood of 78 percent. Evidently the two quantities used in figure 6 are not as sensitive to the presence of naphthenic rings as the Lorentz-Lorenz specific refraction and in many respects these quantities resemble the specific dispersion as closely as they do the Lorentz-Lorenz specific refraction.

3. INCREASE IN HYDROGEN ATOMS PER MOLECULE ON HYDROGENATION

It is now in order to examine by a fundamental method the conclusions drawn from the specific-dispersion and specific-refraction data. Ten fractions from series *C* and three fractions from series *B* were completely hydrogenated, their physical properties recorded, and evidence produced to show that the hydrogenation to naphthenes

was substantially complete and that there was no loss of carbon atoms in the hydrogenation process [4]. For such fractions the difference in x values (from the expression C_nH_{2n+x}) before and after hydrogenation (except for olefinic unsaturation and possible small errors due to the removal of sulfur, nitrogen, and oxygen in the hydrogenation process, which will be considered later) is a measure of the aromatic content.[6]

In the lower half of figure 7 are plotted the x values for the fractions from series C with respect to the percentage extracted both before and after hydrogenation. Unfortunately, after the determination of its physical properties, a sufficient quantity of the important fraction represented by 93.6 percent was not available for hydrogenation. This fraction had a specific dispersion value of 97, which would indicate that it was substantially naphthenic. Nevertheless, it is thought that

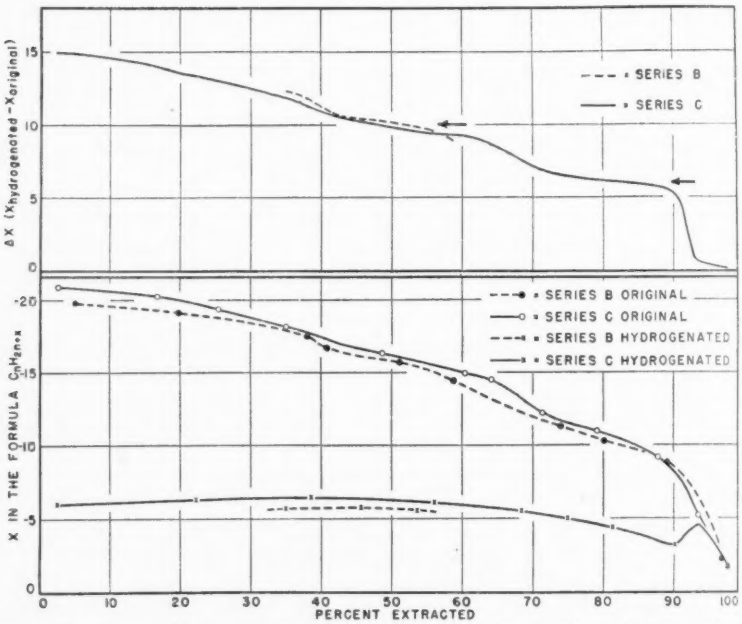

FIGURE 7.—*Lower half: x in the formula C_nH_{2n+x} for fractions before and after hydrogenation; upper half: Increase in hydrogen atoms per molecule on hydrogenation.*

it contained a small amount of aromatic hydrocarbons because its x value, determined experimentally, was −5.2 and that obtained from its specific refraction −3.9. The true value, were it free from aromatic hydrocarbons, would probably lie between these values, and the value −4.6 is believed to be nearly correct. Consequently, the curve for x (hydrogenated) is drawn through this point.

For series B the x (original) value is also plotted over almost the entire range, while the x (hydrogenated) value is given only in a region of particular interest for this series. In the upper half of the same figure is plotted the difference in the x values after and before hydrogenation, $\Delta x = (x \text{ hydrogenated} - x \text{ original})$, which is the in-

[6] Vlugter, Waterman, and Van Westen [11] have used this method extensively.

crease in the number of hydrogen atoms per molecule on hydrogenation. For series *C* this curve shows a nearly horizontal portion from about 88 to 71 percent, in which Δx varies from 5.7 to 6.8. This is considered definite proof that this material consists principally of 1-ring aromatic hydrocarbons and the necessary naphthenic rings and aliphatic side chains.

In the region from 71 to 61 percent there is a rapid increase in Δx to the value 9.2. From 62 to 44 percent there is some indication of a plateau, the Δx value increasing only to 10.5 at 44 percent. The corresponding plateau for series *B* in the region from 56 to 44 percent is slightly more pronounced and the Δx value varies only from 9.6

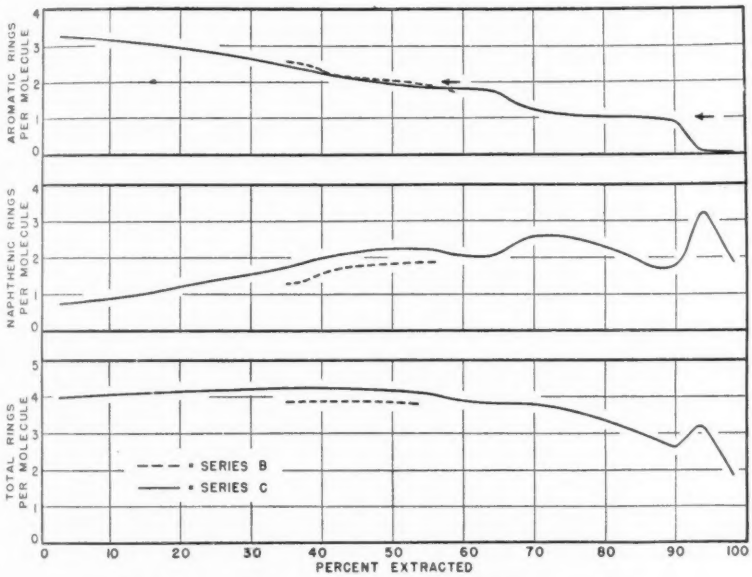

FIGURE 8.—*Rings per molecule of petroleum fractions.*

Lower curve: Total rings per molecule; middle curve: Naphthenic rings per molecule; top curve: Aromatic rings per molecule.

to 10.5. Doubtless, the plateau is associated with 2-ring aromatic hydrocarbons, and the fact that Δx for this plateau is approximately equal to 10 instead of 12 is considered strong evidence that in these hydrocarbons the aromatic rings are linked through two common carbon atoms. If the specific dispersion values are considered in conjunction with the values for Δx, the evidence appears to be conclusive that the aromatic rings are condensed. For example, fraction *C–19*, represented by 53.7 percent with 25.1 carbon atoms, has a specific dispersion value of 190 and a Δx value equal to 9.5. As can be seen from figure 3, it lies reasonably close to the curve for condensed 2-ring aromatic hydrocarbons. If this fraction were composed of rings linked through nonbenzenoid carbon atoms, its specific dispersion would be much lower, about 154, and its Δx value much higher, 12. It is, of course, possible that small amounts of aromatics with noncondensed rings do exist in these fractions, but, if any, the percentage must be small. In figure 8, three curves are given: The

lower curve gives the total number of rings per molecule, the intermediate curve the number of naphthenic rings per molecule, and the upper curve the number of aromatic rings per molecule. The calculation of the number of aromatic rings is based on a change in x value of 6 for the first ring hydrogenated and of 4 for each succeeding ring. This method of calculation assumes that all of the aromatic rings are condensed, an assumption, evidently, reasonably close to the truth. The number of naphthenic rings is given by the difference between the total number and the number of aromatic rings per molecule.

It is interesting to note that even the most soluble fractions with about 3 aromatic rings per molecule contain, on the average, nearly 1 naphthenic ring per molecule. It is evident that the minimum in specific refraction occurring at 72 to 69 percent, to which attention has already been directed, corresponds exactly with the maximum in naphthenic rings per molecule. In all other respects these curves bear out the conclusions drawn from the specific dispersion and specific refraction curves. It will be seen that the remaining physical properties can be interpreted logically on the basis of these same conclusions. It should be emphasized that these fractions are not composed of aromatic hydrocarbons with 1, 2, and 3 aromatic rings mixed with polynuclear naphthenes but that the naphthenic and aromatic rings are contained in the same molecule.[7]

4. SULFUR, NITROGEN, AND OXYGEN CONTENT

At the bottom of figure 9 is given the variation in the total percentage of elements other than carbon and hydrogen, as obtained from the combustion analyses for series *B* and *C*. The upper curves show the variation in sulfur, nitrogen, and oxygen content for series *C*. Several features of these curves are of interest. The nitrogen is concentrated predominantly in the first 10 percent extracted, the sulfur and oxygen, on the other hand, are spread throughout the entire extraction series with the exception of the residue. There is a maximum in the sulfur content, not, as might have been expected, in the first several percent extracted, but somewhere in the region between 20 and 40 percent. Another small but definite maximum in the sulfur content occurs in the neighborhood of 88 percent extracted. The oxygen content also shows a small but definite maximum in this region. This maximum in sulfur and oxygen content corresponds with monocyclic aromatics with the minimum number of naphthenic rings found (1.6), and the decrease in sulfur and oxygen content at slightly lower percentages extracted is associated with increase in the number of naphthenic rings. No explanation is offered for the maximum in sulfur content in the region from 20 to 40 percent. It does not seem probable that sulfur so modifies the solubility of all types of hydrocarbon molecules with which it is combined that it can ever be concentrated by solvent extraction into one narrow region.

[7] Consider a fraction with the formula $C_{30}H_{52}$, which after hydrogenation, has the formula $C_{30}H_{58}$. In 100 molecules of this fraction there are 100 naphthenic rings and 100 aromatic rings. It is apparent that this fraction could not be composed of equimolar portions of the monocyclic aromatic $C_{30}H_{44}$ with the monocyclic naphthene $C_{30}H_{60}$, since 100 molecules of such a mixture would contain only 50 aromatic and 50 naphthenic rings. The fraction could, however, be composed of an equimolar mixture of a dicyclic naphthene $C_{30}H_{58}$ with a dicyclic homologue of diphenyl $C_{30}H_{46}$. Such a mixture would have the empirical formula $C_{30}H_{52}$ and 100 molecules would contain 100 naphthenic and 100 aromatic rings. The coexistence of a 2-ring naphthene and a 2-ring aromatic in extensively extracted fractions like those described above is, however, not possible because of their different solubilities (see aniline point curves for 2-ring naphthene hydrocarbons and 2-ring aromatic hydrocarbons in fig. 13).

Instead, it seems probable that the hydrocarbon portion of the molecule plays a predominant part in governing the solubility of the entire molecule, and consequently the regions in which sulfur is concentrated by extraction depend largely on the type of the hydrocarbon portion of the molecule with which it is combined. As a matter of fact, for the fraction from series *C*, which contains the largest amount of sulfur, the average number of atoms per molecule is 0.14 for sulfur, 0.02 for nitrogen, and 0.15 for oxygen. These are to be compared with hydrogen and carbon atoms to the number of 23.2 and 26.1, respectively.

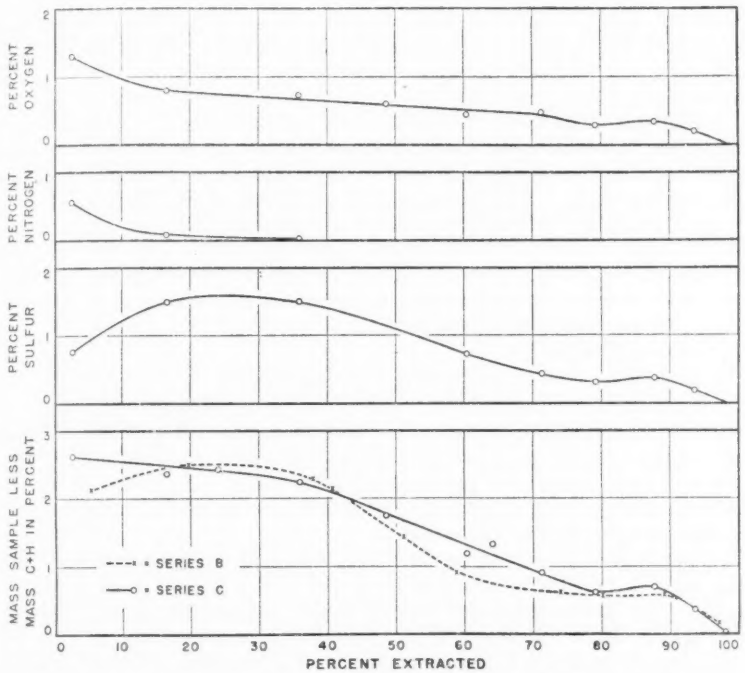

FIGURE 9.—*Sulfur, nitrogen, and oxygen content of petroleum fractions.*

In a preceding section it was pointed out that the removal of sulfur, oxygen, and nitrogen in the hydrogenation process might cause a change in the value of Δx and introduce an error in the calculation of the aromatic content. If the nitrogen, sulfur, and oxygen through all their valencies were linked only to carbon, their removal and the substitution of hydrogen in their place would result in an absorption of three, two, and two atoms, respectively, for each atom of nitrogen, sulfur, and oxygen removed. If, however, the sulfur and oxygen were attached by one valence to carbon and the other to hydrogen, the removal of these elements in the hydrogenation process would cause no change in hydrogen content. In the case of the removal of nitrogen, if two of the valencies were attached to hydrogen

and only one to carbon, a decrease in hydrogen content would occur. Assuming that all the valencies of the sulfur, nitrogen, and oxygen are linked to carbon, for the two fractions in series C represented by 79 and 49 percent extracted, it is possible to attribute changes in Δx of 0.22 and 0.46 to the removal of these elements. The actual change in Δx attributable to this source is likely to be much smaller.

5. OLEFINIC UNSATURATION

Halogen numbers were not determined on any of these fractions, since such determinations are without significance as a means of estimating olefinic unsaturation when applied to mixtures containing aromatic hydrocarbons of high molecular weight. Even methods by which the amount of halogen substituted can be determined and corrected for, give erroneous results with polynuclear aromatics which add halogens. However, although the fractions may contain a small amount of material with olefinic unsaturation, it is evident that the results obtained in section 3 cannot logically be explained as due to such unsaturation. For example, the addition of six atoms of hydrogen per molecule on hydrogenation would require the presence of *exactly* three olefinic double bonds per molecule. In view of the fact that there are no plateaus in the Δx curve showing the addition of two and four hydrogen atoms, corresponding to one and two double bonds, the supposition of three olefinic double bonds per molecule is extremely improbable.

6. OPTICAL ROTATION

As with the specific refraction, there is a general similarity in the shape of the specific rotation curves (fig. 10) and maxima and minima occur at about the same percentages extracted. Minima in specific rotations and maxima in specific refractions occur at the same percentages and/the converse is true also.

Attention has already been directed to the coincidence for the water-white oil of a minimum in refraction with a maximum in optical rotation [2]. In that case, however, only one maximum in rotation was discovered. It is apparent that there is an overlapping of the least soluble fractions from this extraction with the most soluble fractions of the water-white oil, and the maximum in rotation of the water-white oil corresponds with the maximum in rotation occurring with this oil in the neighborhood of 93 percent extracted. Considering series C, there is a sharp increase in specific rotation from 98.2 to 93.6 percent, which shows that in this naphthenic material the rotation increases as the number of naphthenic rings increase. The minimum at 90 percent corresponds with the 1-ring aromatic material with the minimum number of naphthenic rings (1.6). The rotation then increases and reaches another maximum in the neighborhood of 68 percent extracted. This increase is associated with an increase in the number of naphthenic rings; in this case, the addition of naphthenic rings to a 1-ring aromatic.

The decrease in rotation from 68 to lower percentages extracted is associated with the transition from 1-ring aromatic hydrocarbons to hydrocarbons with 2 or more aromatic rings and a smaller number of naphthenic rings per molecule.

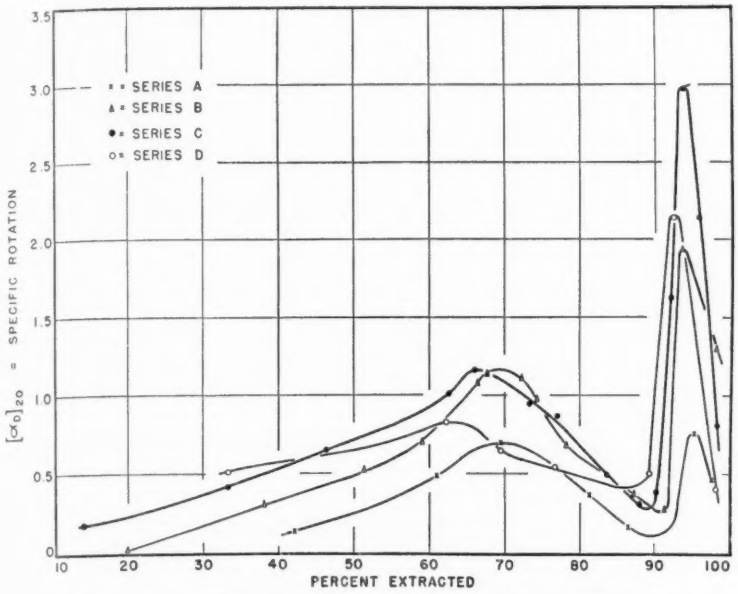

FIGURE 10.—*Specific optical rotation of petroleum fractions.*

In figure 11 the specific optical rotation of the fractions from series *C* has been plotted before and after hydrogenation. It will be observed that the shape of the curve is the same after as before hydro-

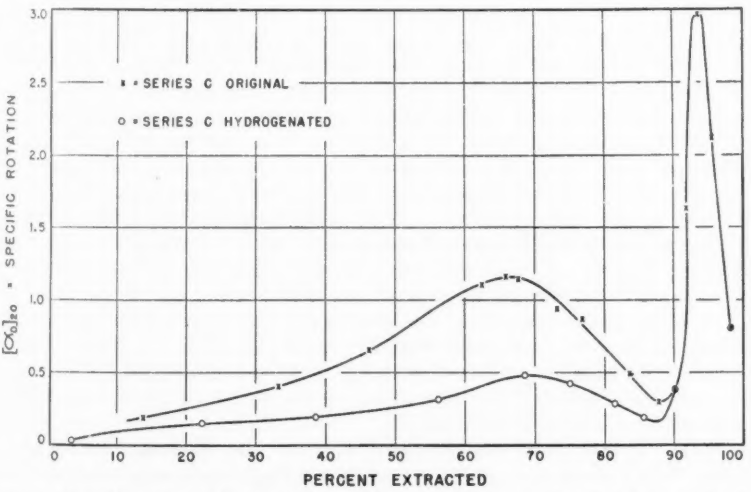

FIGURE 11.—*Specific optical rotation of fractions from series C before and after hydrogenation.*

genation, a maximum again occurring in the neighborhood of 68 percent. However, the magnitude of the rotation has been markedly reduced for all the fractions up to 86 percent; a result which is to be expected, since hydrogenation probably would reduce the centers of

asymmetry and also reduce the polarity of the molecules. The fraction represented by 90 percent shows the same rotation before and and after hydrogenation. This fraction is composed of a mixture of 1-ring aromatic hydrocarbons with a small quantity of polycyclic naphthenes. Since on hydrogenation there was no change in its rotation, it appears that the naphthenic material alone was responsible for its rotation, the aromatic material contributing nothing. Consequently, if a sharper separation of the purely naphthenic material from the material containing 1 aromatic ring could be obtained, a higher peak for the optical rotation should result in the region around 93.6 percent and a lower depression around 90 percent for the first of the aromatic material. The residue represented by 98.2 percent showed the same rotation before and after hydrogenation. An insufficient amount of the fraction represented by 93.6 percent was available for hydrogenation. However, this fraction was preponderantly naphthenic, and hydrogenation would doubtless not have affected its rotation.

André and Bloch [12], André [13], and Roche [14], in investigating the optical activity of lubricating oils effected very considerable changes in the optical rotation by solvent extraction, and found for a number of oils from different sources that the maximum rotation occurred for fractions with empirical formulas in the neighborhood of $C_{28}H_{50}$. Since this formula does not differ from that of the 4-ring naphthene cholestane, these authors consider their results as partial confirmation of the hypothesis of Marcusson, who suggested that the sterols might be the source of material for optically active compounds in petroleum. However, these authors have given no evidence to indicate that their fractions were purely naphthenic and they may well have contained considerable aromatic material.

In this investigation the fraction with the greatest specific rotation $[\alpha]_D^{20}=+2.97$ was found in series *C* and is represented by 93.6 percent extracted. This fraction is predominantly naphthenic (see fig. 8) and has on the average 29.6 carbon atoms and about 3.2 naphthenic rings to the molecule. This fraction occurs in the extraction series between aromatic material with low rotation and naphthenic material with a smaller number of rings and low rotation. It seems entirely probable that better separation of the small amount of aromatic material from this fraction and of the naphthenes with a smaller number of rings would have yielded some 4-ring naphthenes with still higher rotation. In this connection, see also the discussion on the rotation of the hydrogenated fraction represented by 90 percent.

In the water-white oil [1] the fraction having the greatest rotation $[\alpha]_D^{20}=+1.96$ has the empirical formula $C_{27.7}H_{52.6}$. This fraction is purely naphthenic and contains 2.4 rings per molecule. Our results are thus substantially in agreement with those of André and Bloch [12], André [13], and Roche [14].[8]

However, new information results from the present investigation which shows that the optically active compounds are concentrated, also by solvent extraction, in another region. The second region most optically active occurs from 68 to 66 percent extracted for series *C*, for which $[\alpha]_D^{20}$ was 1.14 to 1.16. Fractions in this region consist

[8] A maximum in optical activity with $[\alpha]_D=8$ has been reported by Engler and Steinkopf [15] for the fraction of an Argentine (Mendoza) crude distilling at 216° C at 0.5 mm Hg. Such a fraction might be expected to have somewhere in the neighborhood of 28 carbon atoms per molecule.

substantially of 1 aromatic ring with about 2.6 naphthenic rings per molecule. The similarity between these fractions and cholestane is apparent, since the dehydrogenation of one 6-membered ring in cholestane results in a hydrocarbon with 1 aromatic and 3 naphthenic rings.

Although the results so far considered are in agreement with the supposition that the sterols with 27 to 30 carbon atoms might be the source of the optically active compounds in petroleum, another factor is to be considered. In the water-white oil [1], which had been repeatedly distilled before extraction, fractions which still had appreciable optical rotation were found considerably removed both in boiling point and in the number of carbon atoms from the fraction with the maximum activity. Thus, although the maximum activity, with specific rotation equal to 1.96, occurred for a fraction with 27.7 carbon atoms and a boiling point of 204° C at 1 mm Hg, a fraction with 37.4 carbon atoms and a boiling point of 269.5° C at 1 mm Hg had a specific rotation of 0.51. For a material thoroughly fractionated by distillation, it seems quite impossible that a sufficient quantity of the hydrocarbons with high rotation from the fraction boiling at 204° C could be present in the fraction boiling at 269.5° C to account for its still very considerable rotation. The present investigation with material extensively distilled shows optical rotation in fractions with boiling points at 1 mm Hg from 185° to 260° C and covering a wide range of carbon atoms (23 to 34). Thus, if the sterols alone are to be considered as the source material of optically active compounds in petroleum, it is necessary to postulate the generation from them of compounds of higher and lower molecular weight.

7. ANILINE POINTS

In figure 12 is a plot of the aniline points of the fractions from series *A*, *B*, *C*, *D*, and *E*, with respect to the percentages extracted. As with the other physical properties, there are pronounced breaks in the slope of these curves occurring at approximately the same percentages extracted.

In figure 13, curves are drawn which show the aniline points with respect to the number of carbon atoms for a number of different types of hydrocarbons. The upper curve, $x=+2$, is based on the normal paraffin hydrocarbons. The values for the paraffins of lower molecular weight are those reported by Evans [16], who converted most of these values from the data of Shepard, Henne, and Midgley for critical solution temperatures [17]. The data for the two paraffins of higher molecular weight, *n*-nonacosane (122.0° C) and *n*-dotriacontane (128.0° C) were obtained in this laboratory. The value 127.6° C for the critical solution temperature in aniline for dotriacontane was recently reported by Tilitsheyev [18]. Immediately below the curve for the normal paraffins are drawn curves which show the aniline points of naphthenes containing 1, 2, 3, and 4 rings, respectively. The aniline points for the monocyclic and dicyclic naphthenes of low molecular weight on which one end of each curve is based, are those reported by Evans [16]. In the region of high molecular weight, the curves are based on the naphthene fractions of the water-white oil [1] prepared by extraction and on the fractions obtained by hydrogenation [4]. In

determining the location of these curves, there were used only fractions with specific dispersions of 100 or less, which were considered substantially free of aromatic hydrocarbons. Mikeska [7] gives aniline points for two monocyclic and one dicyclic naphthene of high molecular weight. His values for the two monocyclic hydrocarbons are much lower than the corresponding curve, while the value for the dicyclic hydrocarbon is fairly close to the corresponding curve.

Also shown in the figure is a curve for the homologues of benzene ($x=-6$). The region from 15 to 22 carbon atoms is based on the

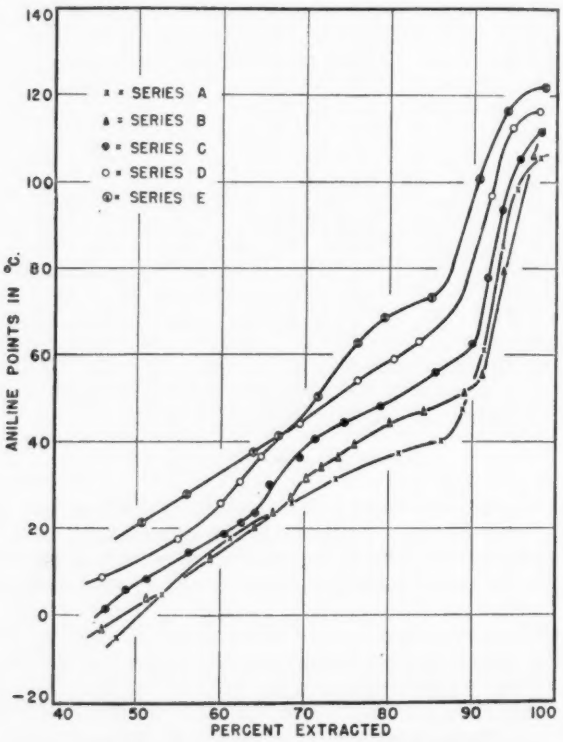

FIGURE 12. *Aniline points of petroleum fractions.*

critical solution temperature data given by Tilitsheyev [18],[9] while from 24 to 60 carbon atoms the data are those of Mikeska [7].

Below this curve, another curve is drawn through Mikeska's [7] data for homologues of tetralin. This curve shows approximately what would be the aniline points of material containing 1 aromatic and 1 naphthenic ring. The lowest curve is based on Mikeska's data for homologues of naphthalene.

The aniline points of fractions from series *C* are also shown in figure 13, and certain fractions of importance to the discussion have been indicated. Considering now series *C*, the fraction represented by 98.2 percent has an x value of -1.83, in fair agreement with that

[9] Evans [16] has pointed out that for many hydrocarbons the critical solution temperatures in aniline usually do not differ as much as 2° C from the aniline points.

expected from the corresponding curve. The fraction is therefore substantially naphthenic. For the fraction represented by 93.6 percent, the x value is -5.2 and the aniline point is 93.6° C. This aniline point is somewhat low for a pure naphthene and indicates, as was expected from the specific refraction data, the presence of a small amount of aromatic material. From 93.6 to 90 percent extracted, transition from substantially naphthenic material to material consisting substantially of hydrocarbons with one aromatic ring occurs; the aniline point drops sharply and has a value of 55.9° C for the fraction represented by 86 percent extracted. As can be seen from figure 8, this material contains 1 aromatic ring and an average of

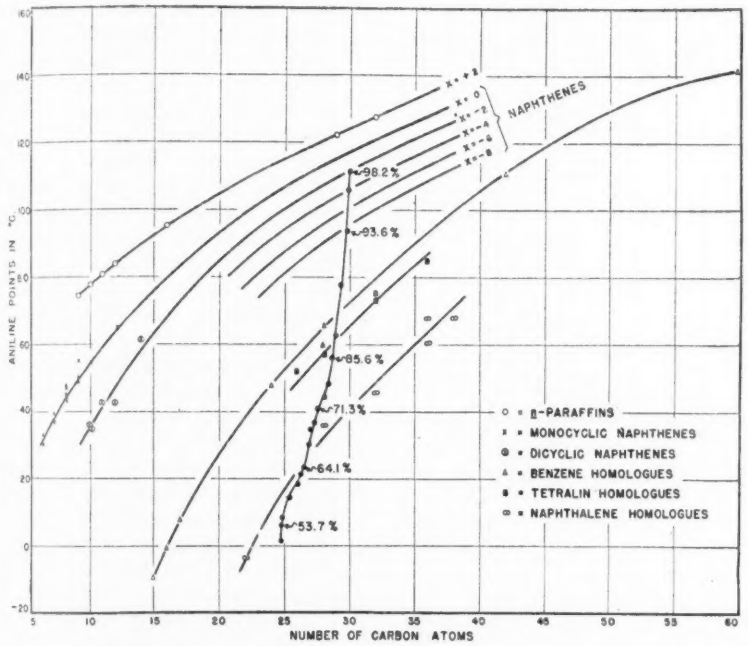

FIGURE 13. *Aniline points of various types of hydrocarbons with respect to the number of carbon atoms per molecule.*

1.8 naphthenic rings. It is evident that its aniline point is in agreement with this composition.

From 86 to 71 percent extracted, the aniline points are in agreement with the conclusions drawn from figure 8, that is, that this material contains 1 aromatic ring with increasing numbers of naphthenic rings. The sharp break occurring in the aniline point curve for series C, (fig. 12) between 71.3 and 64.2 percent extracted, corresponds exactly with the transition to 2-ring aromatic hydrocarbons (see fig. 8). The aniline point of the fraction represented by 64 percent extracted is close to the curve for homologues of naphthalene. The aniline points of the fractions from 64.2 to 53.7 percent extracted are somewhat lower than those for aromatic hydrocarbons with 2 condensed rings, but this is exactly what would be expected since this material also contains some naphthenic rings.

8. VISCOSITY AND THE TEMPERATURE COEFFICIENT OF VISCOSITY

In figures 14, 15, and 16 have been plotted the viscosity at 100° and 210° F and the kinematic-viscosity index for the fractions from 50 to 100 percent extracted, for series *B*, *C*, *D*, and *E*. For each series, both at 100° and 210° F, the viscosity is a minimum for one fraction in the neighborhood of 90 percent extracted, and a maximum for the next fraction, which is represented by about 94 percent. The viscosity index (a measure of the temperature coefficient of viscosity) varies in the opposite manner, being a maximum at 90 percent and a minimum at 94 percent. Attention has already been directed to this unusual behavior in connection with the investigation of the water-white oil [2], in which some of the first fractions from the extractors showed the same abnormal behavior. It is evident that the last few fractions at the end of the present extraction and the first few fractions at the beginning of the extraction of the water white oil [1, 2] are of the same composition, and the explanation given there accounts also for the unusual behavior noticed here. Mikeska [7] has pointed out that for 1- and 2-ring compounds the viscosity depends (other things being equal) on the percentage of rings in the molecule, and that aromatics with 1 and 2 rings have slightly lower viscosities than the corresponding naphthenes. (As will be seen later, this statement is probably not applicable for compounds containing 3 or more rings.) As can be seen from figure 8, there is an increase in the total number of rings in going from the aromatic material at 90 percent extracted to the naphthenic material at 94 percent, and it is to this increase in rings that the increased viscosity and decreased viscosity index are due.

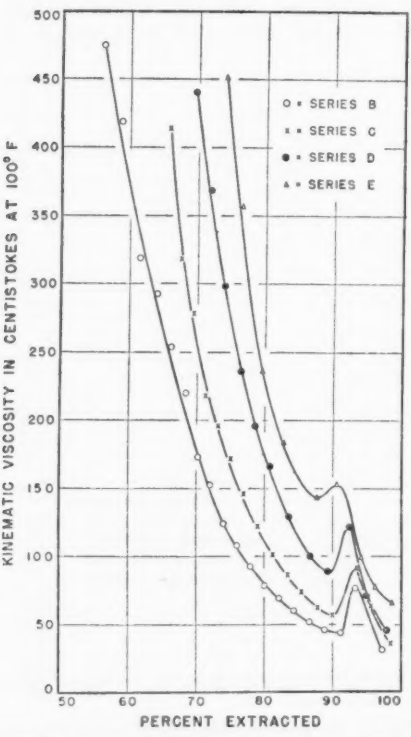

FIGURE 14.—*Kinematic viscosity at 100° F of petroleum fractions.*

In an earlier publication [2], the authors speculated on the possibility of obtaining from petroleum aromatic material of high viscosity index. As shown here, material with 1 aromatic ring does exist but the percentage is not great, and the viscosity index of some of it, though higher than that of the naphthenic material which immediately follows it in the extraction series, attains the value of only 70. This is probably because the aromatic rings instead of being attached only to aliphatic side chains are attached also to naphthenic rings, the

fraction from series *C* with the highest viscosity index, 69 to 70, containing, in addition to 1 aromatic ring, an average of from 1.6 to 1.8 naphthenic rings per molecule.

Although there are some small fluctuations in the viscosity characteristics at lower percentages extracted, these may be due to experimental error—and no pronounced abnormalities are noticed in the region around 70 percent where the transition from 1-ring to 2-ring aromatic hydrocarbons occurs.

In figures 17, 18, and 19, the viscosities and viscosity indices of the fractions from series *C* are compared before and after hydrogenation. Considering figures 17 and 18, it is apparent that the residue represented by 98.2 percent (as was to be expected since this material was already naphthenic) shows on hydrogenation no change in viscosity either at 100° or 210° F. For the fraction represented by 90 percent there is a slight increase in viscosity on hydrogenation. Since this fraction is composed of a 1-ring aromatic with about 1.6 naphthenic rings to the molecule, this result is in conformity with Mikeska's [7] observation that naphthenes with 1 and 2 rings have viscosities slightly higher than those of the corresponding aromatics. However, from 90 to 0 percent extracted, the viscosity of the hydrogenated fractions becomes increasingly less than the original fractions, and in the neighborhood of 3 percent extracted, the viscosity at 100° F after hydrogenation is about 1 percent of its original value. This result was unexpected, and could not have been predicted from the published data on 1- and 2-ring compounds.

It appears that the hydrogenation of 1 or more aromatic rings,

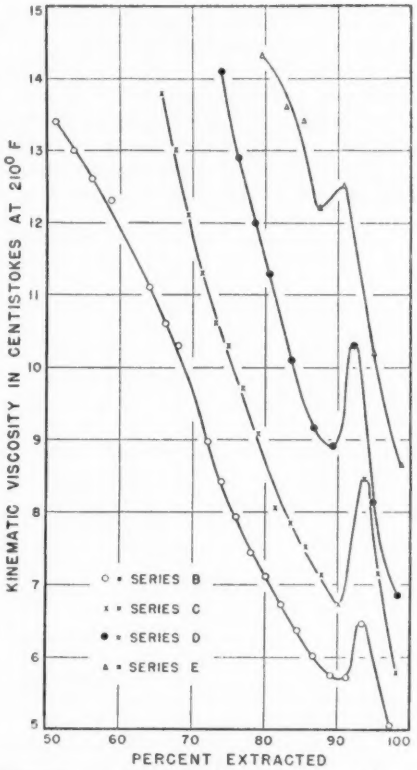

FIGURE 15.—*Kinematic viscosity at 210° F of petroleum fractions.*

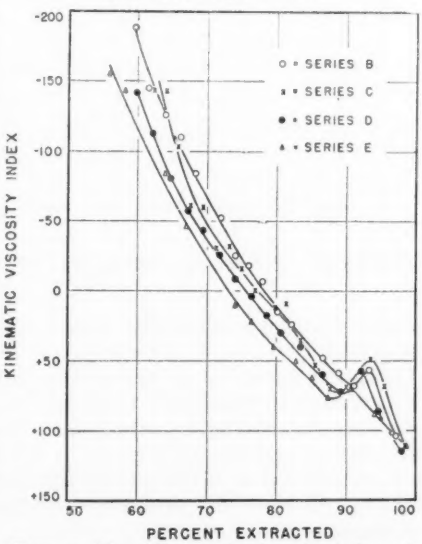

FIGURE 16.—*Kinematic-viscosity index of petroleum fractions.*

when those rings are attached to 2 or more naphthenic rings (probably in the condensed form), results in a decrease in viscosity, and the decrease in viscosity becomes greater, the greater the number of aromatic rings hydrogenated. These types of hydrocarbons should be synthesized and their viscosities measured to establish definitely the validity of this conclusion. Considering now figure 19, the viscosity index of the residue represented by 98.2 percent is (within the limits of error) about the same before and after hydrogenation. No appre-

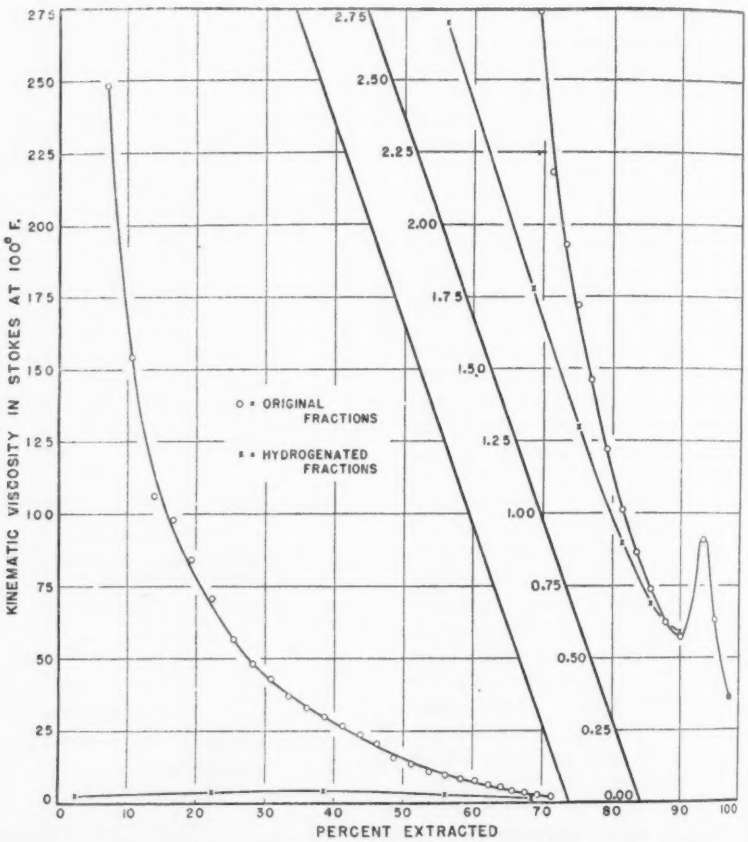

FIGURE 17.—*Kinematic viscosity at 100° F of fractions from series C before and after hydrogenation.*

ciable change in viscosity index has occurred for the fractions represented by 90 and 85.6 percent—a result in agreement with Mikeska's [7] observations for 1- and 2-ring compounds. However, from 85.6 to 0 percent extracted, the viscosity indices of the hydrogenated fractions became increasingly greater than the viscosity indices of the original fractions, and the difference in viscosity indices is very great in the neighborhood of 3 percent extracted. The explanation given for the change in viscosity probably accounts also for the change in viscosity indices.

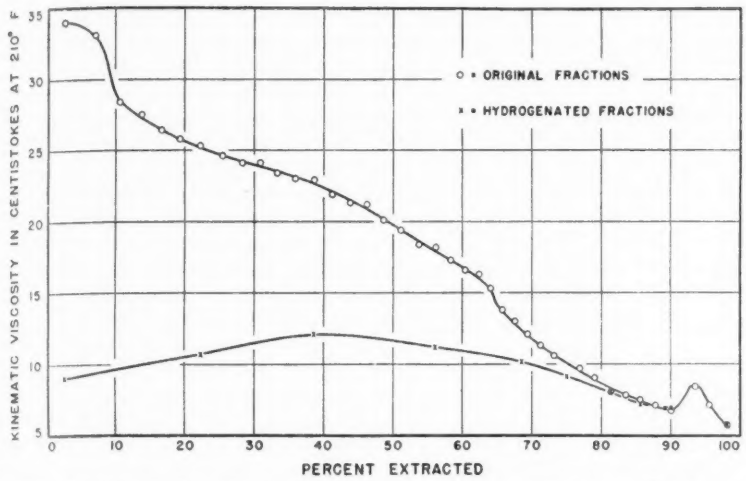

FIGURE 18.—*Kinematic viscosity at 210° F of fractions from series C before and after hydrogenation.*

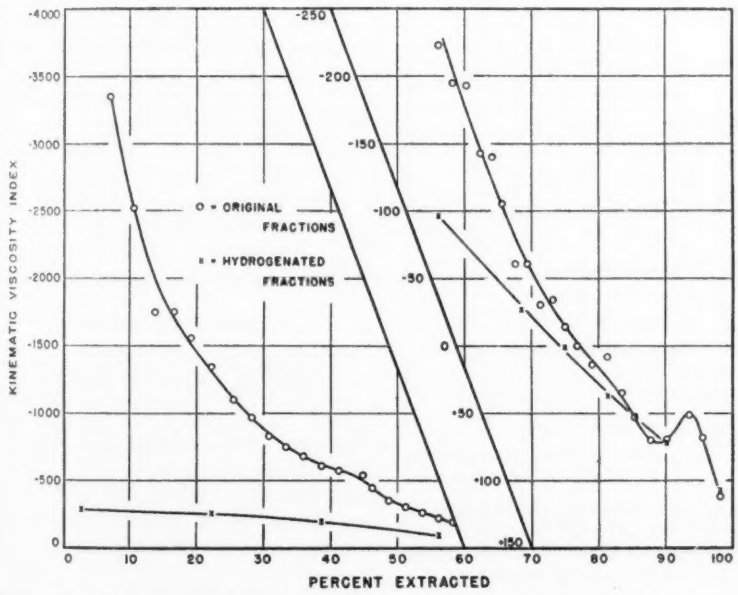

FIGURE 19.—*Kinematic-viscosity index of fractions from series C before and after hydrogenation.*

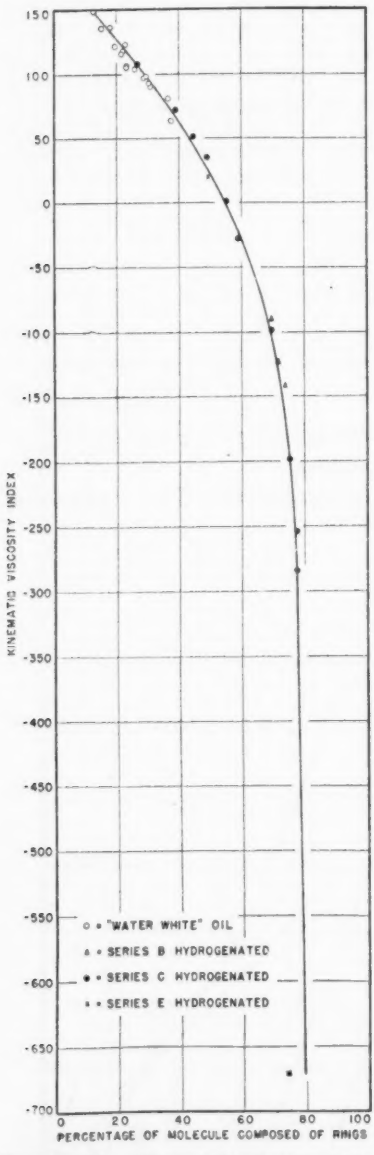

FIGURE 20.—*Kinematic-viscosity index of hydrogenated and of water-white oil fractions with respect to the percentage of the molecule composed of rings.*

Davis and McAllister [19] have shown that a linear relationship exists between the viscosity index of an aromatic-free oil and the percentage of carbon atoms in naphthenic rings. In figure 20, the fraction of the molecule composed of rings has been plotted with respect to the viscosity index for the water-white oil and for the fractions resulting from the hydrogenation of the extract fractions. Only those water-white oil fractions with specific dispersions of 100 or less, and therefore substantially free from aromatic hydrocarbons, have been used in this plot. The total number of rings possible has been calculated on the assumption of condensed 6-membered rings, that is, allowing six carbon atoms for the first ring and four carbon atoms for each succeeding ring. This material is not composed entirely of 6-membered uncondensed rings since a calculation on this supposition leads, for some of the fractions, to over 100 percent in ring form. The points fall close to a smooth curve which permits a study of the relationship at much lower viscosity indices than that given by Davis and McAllister [19]. The relationship is not linear and in the region where the fraction of the molecule in rings changes from 70 to 80 percent, the decrease in viscosity index is very rapid.

9. BOILING POINT

In figure 21 the boiling points at 1 mm Hg of the fractions from series *B* and *C*, before and after hydrogenation, are plotted against the percentages extracted. The boiling points of the original fractions from one series before hydrogenation are substantially constant. From 100 to 90 percent extracted, there is no change in boiling point on hydrogenation (within the accuracy of these measurements). From 90 to 0 percent extracted, however, there is a decrease in boiling point on hydrogenation, and the boiling point of the hydrogenated fraction (series *C*) represented by 2.6 percent is 50° C lower than that of the

original. This drop in boiling point is in agreement with the well-known fact that polynuclear naphthenes have much lower boiling points than the corresponding aromatic hydrocarbons. *Trans*-decahydronaphthalene, for example, has a boiling point (760 mm) 33° C lower than that of naphthalene.

In figure 22 is given a plot of the boiling points with respect to the number of carbon atoms for the hydrogenated fractions and for the water-white oil fractions [1] for which the specific dispersion is less than 100. It will be noticed that a straight line represents the data fairly well, and only in about four cases do the points fall farther from thr line than could be accounted for on the basis of the precision of these determinations. Two curves are given for the extract fractions foe $x=-14$ and $x=-18$. These represent, within about $\pm 3°$ C, the boiling points of the extract fractions with corresponding values of x.

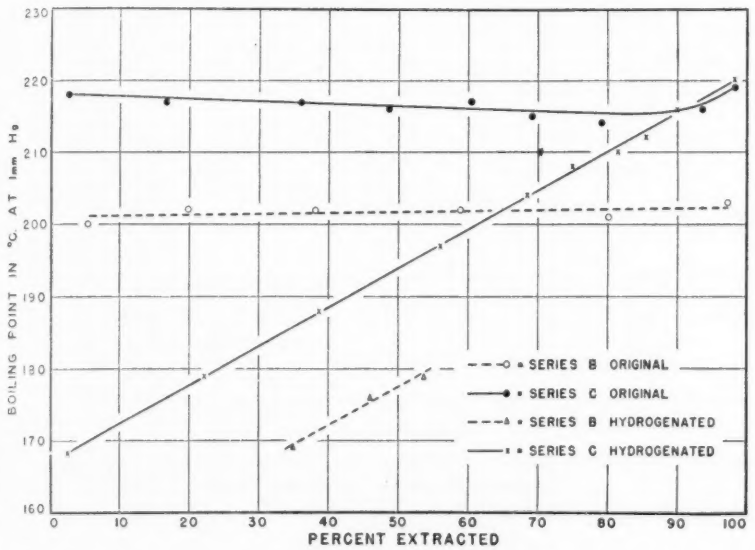

FIGURE 21.—*Boiling points of fractions from series B and C before and after hydrogenation.*

Also included in this figure are the boiling points determined in this laboratory on some synthetic compounds, all of which, with the exception of dotriacontane, were kindly furnished by L. A. Mikeska [7]. It will be noted that the boiling point of compound number 7, *n*-dotriacontane at 251° C, is 16° higher than that of the naphthene fractions with the corresponding number of carbon atoms. This result is not unreasonable, since the normal compounds have higher boiling points than those with branches and it is probable that the difference of 16° is due both to the rings and side chains which these fractions contain. Compound 1 consists of a benzene ring with a normal aliphatic side chain. Its boiling point is only slightly higher than its x value would indicate. In the case of compound 2 the boiling point is higher than its x value would indicate. Here the high boiling point may be due to the long unbranched side chain. Compound 3 has a

boiling point about what would be expected. In this case, the side chain is branched and contains an olefinic linkage. Compounds 5 and 6 are homologues of tetralin and decalin with a singly branched side chain. It is surprising to see the boiling point of the decalin homologue higher than that of the tetralin homologue, and this result is probably in error. If the boiling point of compound 6 had fallen just below that of compound 5, it would be in good agreement with the naphthene fractions.

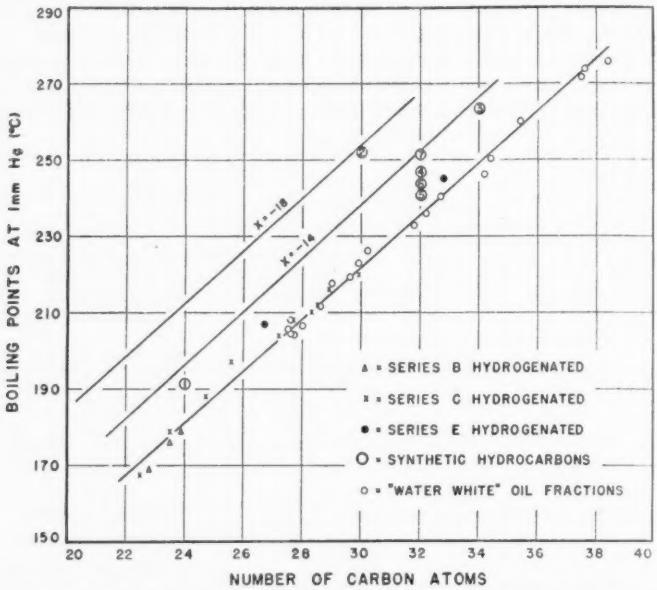

FIGURE 22.—*Boiling points of petroleum fractions and synthetic hydrocarbons with respect to the carbon atoms per molecule.*

The numbers represent values for the hydrocarbons as follows:

1. 1-Phenyloctadecane
2. 1-(*p*-diphenyl)-octadecane
3. (5)-(*p*-diphenyl)-docosene−5
4. 5-(7-tetrahydronaphthyl)-docosene−5
5. 5-(7-tetrahydronaphthyl)-docosane
6. 5-(2-decahydronaphthyl)-docosane
7. *n*-Dotriacontane

IV. CONCLUSION

As a result of the work on the water-white oil and on the extract material, it is possible to obtain an approximate estimate of the quantities of the various types of hydrocarbons in the lubricant fraction of this midcontinent petroleum. Excluding the wax and the asphaltic portions, the oil contains (1) about 60 percent of naphthenes with from 1 to 3 rings per molecule—a very small amount of material containing 4 naphthenic rings per molecule is probably present also; (2) about 15 percent of material with 1 aromatic ring and with from 1 to 3 naphthenic rings per molecule and with this material is associated a small amount of sulfur and oxygen compounds; (3) about 14 percent of material with 2 aromatic rings (linked through two common carbon

atoms) together with about 2 naphthenic rings per molecule, and with this material is associated a small amount of sulfur and oxygen compounds; (4) about 11 percent of material with more than 2 aromatic rings per molecule (each probably linked through two common carbon atoms) together with 1 or 2 naphthenic rings per molecule, and with this material is associated some sulfur, nitrogen, and oxygen compounds.

The authors desire to express their gratitude for the advice and encouragement of F. D. Rossini.

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WASHINGTON, July 25, 1938.

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RESEARCH PAPER RP1146

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EFFECT OF PURIFICATION TREATMENTS ON COTTON AND RAYON

By Ruby K. Worner and Ralph T. Mease

ABSTRACT

This paper is concerned with the effect on cotton, and also on cuprammonium and nitrocellulose rayons, of the Corey and Gray modification of the American Chemical Society method for the preparation of "standard cellulose" from cotton. When the fibers were subjected to successive cycles of treatments, each of which consisted in separate extractions with alcohol, ether, and a 1-percent solution of sodium hydroxide, a progressive change in the fibers took place. This was evident from the loss in weight of the fibers and the increase in the fluidity of their cuprammonium solution. Low copper numbers were obtained for all the fibers after the first extraction with alkali. Repeated treatments had no pronounced effect on the alpha-cellulose content of the cotton. Alcohol and ether had no measurable effect other than the removal of soluble material during the first cycle.

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I. INTRODUCTION

Some treatment for the removal of natural noncellulosic materials from cotton is necessary in preparing this fiber for certain studies relating to its use in the textile industry. A method for the removal of these impurities should be one that results in minimum damage to the fiber.

The method for the preparation of "standard" cotton cellulose of the Cellulose Committee, American Chemical Society, as modified by Corey and Gray[1] comprises the successive extractions of raw cotton with alcohol, ether, and a boiling 1-percent solution of sodium hydroxide. Although the resulting product has the characteristics associated with a product of high chemical purity, there is evidence that, aside from the removal of noncellulosic materials, the treatment probably affects certain physical properties of the fiber, as shown by changes in the fluidity of cuprammonium solutions of cellulose fibers caused by treatment with boiling dilute alkali. The measurement of the fluidity of a dispersion of cellulose in cuprammonium solution is particularly

[1] Ind. Eng. Chem. **16**, 853, 1130 (1924).

useful in the early stages of degradation for detecting and following slight changes in the fiber before they are evident from direct measurements[2] of strength. Kanamaru[3] found that when cotton is immersed in boiling sodium hydroxide solutions, the viscosities of cuprammonium dispersions of the resulting products decreased rapidly in the first 7 or 8 hours of treatment, increased somewhat or changed but little in the next few hours, and then gradually decreased with further treatment. Somewhat similar results were obtained by Lewis,[4] who, however, used chemically bleached cellulose fibers in the form of rag and purified sulfite pulps.

The present work was undertaken to provide information on the changes effected by the Corey and Gray procedure on cotton and rayon textile fibers. The effects of each step in the procedure and of repetitions of the cycle of treatments were measured with respect to changes in alpha-cellulose content and copper number, tests previously applied to cotton cellulose purified by the method, and in addition by changes in weight and the apparent fluidity of their solution in cuprammonium. The cycle of treatments was repeated to determine the effect of each on the cellulose and thereby indicate the probable effect of the single cycle prescribed by the method, which cannot be measured directly.

Similar data were obtained for cotton digested in hydrochloric acid of sp gr 1.19, in the manner described by Farr and Eckerson.[5] It is recognized, however, that this treatment is for the purpose of preparing cellulose particles from cotton membranes and is not intended to produce pure cellulose in fiber form.

II. MATERIALS

The raw cotton used in these experiments was furnished by the Bureau of Agricultural Economics, United States Department of Agriculture. It was of the Acala variety, grown in 1932 at Blytheville, Ark., and was classed as Strict Middling in grade and was $^{31}/_{32}$ inch in staple length. It had been ginned and twice carded but had received no chemical treatments. It may be considered to represent high-grade natural cellulose.

The rayons were 150 denier commercial products obtained direct from the manufacturers and had received no treatments after spinning. The cuprammonium rayon may be considered to represent regenerated cellulose that has undergone the least drastic treatment in manufacture, the nitrocellulose, the most drastic treatment.[6]

III. TEST METHODS

The alpha-cellulose content was determined by the volumetric method of Launer,[7] and the copper number by the method described by Burton and Rasch.[8]

The fluidity of the cuprammonium dispersion of cellulose was measured in accordance wth the recommendations of the Fabrics

[2] J. Textile Inst. **15**, T157 (1924); **16**, T13 (1925); **17**, T145 (1926); **18**, T277 (1927); Charles Dorée, Methods of Cellulose Chemistry (Chapman & Hall, London) and literature cited therein.
[3] Cellulose Ind. (Tokyo) **7**, 149. Abstracts 33 (English) (1931).
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[6] J. Textile Inst. **22**, T121 (1931).
[7] J. Research NBS **18**, 333 (1937) RP979.
[8] BS J. Research **6**, 613 (1931) RP295.

Research Committee (London),[9] except that the concentration of 240 g of ammonia per liter, originally recommended by Clibbens and Geake,[10] was used. The measurements were made at 21°±0.1° C. The results are expressed as fluidity in cgs units (reciprocal poises or rhes) for 0.5-percent solutions of cotton and for 2-percent solutions of rayon.

The percentage loss in weight was calculated on the basis of the weight of the dry sample before the first treatment,[11] which was taken as 100 percent.

IV. EXTRACTION WITH ALCOHOL, ETHER, AND 1-PERCENT SOLUTION OF SODIUM HYDROXIDE

The fibers were first immersed in water at 60° C. and conditioned to constant weight in an atmosphere of 65-percent relative humidity and 21° C. Determinations of the moisture content, fluidity of their cuprammonium solution, copper number, and alpha-cellulose content were made on the conditioned, untreated material.

The three kinds of fibers were subjected five times to a cycle of treatments, each cycle being divided into three steps. Samples were analyzed at the end of each step.

In the first step, the fiber was extracted in a Soxhlet apparatus for 6 hours with alcohol, was air-dried at room temperature, immersed in water at 60° C. for about 5 minutes, and again conditioned to constant weight. The second step was similar to the first except that ether was substituted for the alcohol. In the third step, the material was extracted for 6 hours with a boiling 1-percent solution of sodium hydroxide, thoroughly washed with distilled water, steeped for 2 hours in a 1-percent solution of acetic acid at room temperature, washed with distilled water, and conditioned to constant weight.

This is the Corey and Gray procedure, except for slight modifications of the equipment used for the extractions with alkali and the immersion in water following the extractions with alcohol and ether. These immersions were intended to remove any adsorbed solvent and to permit the specimens to approach a constant weight from a wet condition.

The apparatus shown in figure 1 was used for the extractions with alkali. The fiber was placed in the cheesecloth bag, *D*, and agitated in the cylinder, *A*, which contained about 10 liters of a 1-percent solution of sodium hydroxide. This solution was freshly boiled before the material was introduced, and was kept boiling during the period of the extraction. The position and amplitude of the plunger, *C*, were adjusted so that the cellulose was immersed in liquid at all times. A boiling 1-percent solution of sodium hydroxide was siphoned continually from the cylinder, *B*, to *A* at the rate of about 2.5 liters per hour for 6 hours. The tube, *G*, which was connected to a pump, maintained a constant level in *A* by removing the old solution as rapidly as the fresh was introduced.

With the exception of the first cycle of treatments, alcohol and ether had no significant effect on either the weight of the fibers or on

[9] Report of the Fabrics Research Committee, Department of Scientific and Industrial Research. His Majesty's Stationery Office, London (1933).

[10] J. Textile Inst. **19**, T77 (1928).

[11] Calculated from the moisture content and the weight after coming to equilibrium in an atmosphere of 65-percent relative humidity at about 21° C. The moisture content was determined by heating specimens of the conditioned cotton or rayon in a drying oven at 105° to 110° C to constant weight.

their measured properties. Cotton lost 1.7 percent of its weight in the first cycle, as a result of extraction with alcohol; cuprammonium rayon, 0.1 percent; and nitrocellulose rayon, 0.0 percent. Subsequent extractions with ether had no further effect on the cotton, but the cuprammonium and nitrocellulose rayons lost 0.4 and 0.2 percent in

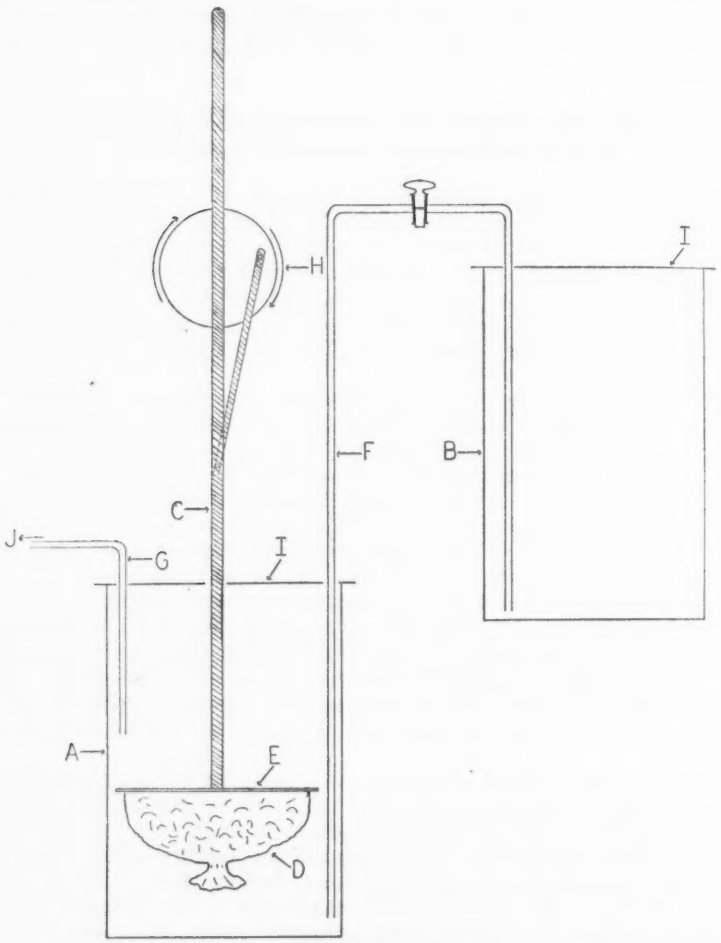

FIGURE 1.—*Apparatus for extracting fibrous materials with a sodium hydroxide solution.*

A and *B*, 16-liter Monel-metal vessels; *C*, Monel-metal plunger; *D*, cheesecloth bag; *E*, perforated disk; *F*, siphon; *G*, overflow tube; *H*, drive-wheel for plunger; *I*, Monel-metal covers; and *J*, to pump.

weight, respectively. The fluidities of dispersions in cuprammonium solutions of the untreated fibers and of the fibers after extraction with alcohol and ether were the same. Except for the losses in weight resulting from extraction with alcohol and ether in the first cycle, all the changes that occurred in a cycle of treatments may be attributed to the action of a boiling 1-percent solution of sodium hydroxide.

The over-all effects of one and five cycles of treatments on the properties of the three kinds of fibers are shown in table 1. At the end of

TABLE 1.—*Effect on cotton, cuprammonium rayon, and nitrocellulose rayon of 1 and 5 cycles of treatments, each including extraction with alcohol, ether, and hot 1-percent solution of sodium hydroxide*

Treatment	Cotton				Cuprammonium rayon			Nitrocellulose rayon		
	Fluidity (0.5% solution)	Copper number	α-Cellulose content	Loss in weight	Fluidity (2% solution)	Copper number	Loss in weight	Fluidity (2% solution)	Copper number	Loss in weight
	Rhes		*Percent*	*Percent*	*Rhes*		*Percent*	*Rhes*		*Percent*
Untreated	1.1	0.01	97.4	-------	4.3	0.5	-------	14.9	2.4	-------
One cycle	2.4	.01	95.7	4.5	5.8	.2	4.5	18.8	.5	16.9
Five cycles	14.9	.01	94.6	12.7	14.7	.1	17.7	25.6	.1	33.6

the first cycle of treatments the fluidities of the treated fibers are somewhat higher than those of the untreated. At the end of the five cycles, all three kinds of fibers have very different properties from the

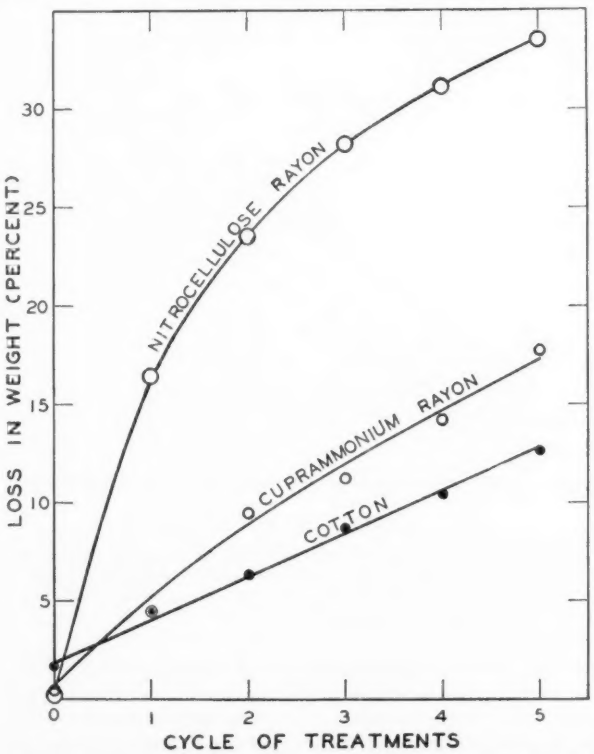

FIGURE 2.—*Loss in weight of cotton, cuprammonium rayon, and nitrocellulose rayon in repeated extractions with alcohol, ether, and 1-percent solution of sodium hydroxide.*

The values given for the 0-cycle represent the loss after the first extraction with alcohol and ether, but before the first extraction with 1-percent solution of sodium hydroxide. The other values represent the cumulative loss at the end of each cycle of treatment.

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untreated fibers. It was also noted that the treated fibers were weaker than the untreated.

Low copper numbers were found for all the fibers after the first extraction with alkali, for the reducing substances in cellulose responsible for its copper number are removed by boiling with alkali.[12]

The values for the alpha-cellulose content of the cotton after one and five cycles are nearly the same, whereas the fluidities are very different.

The loss in weight at the end of each cycle is shown in figure 2, in which the combined effect of the first extractions with alcohol and

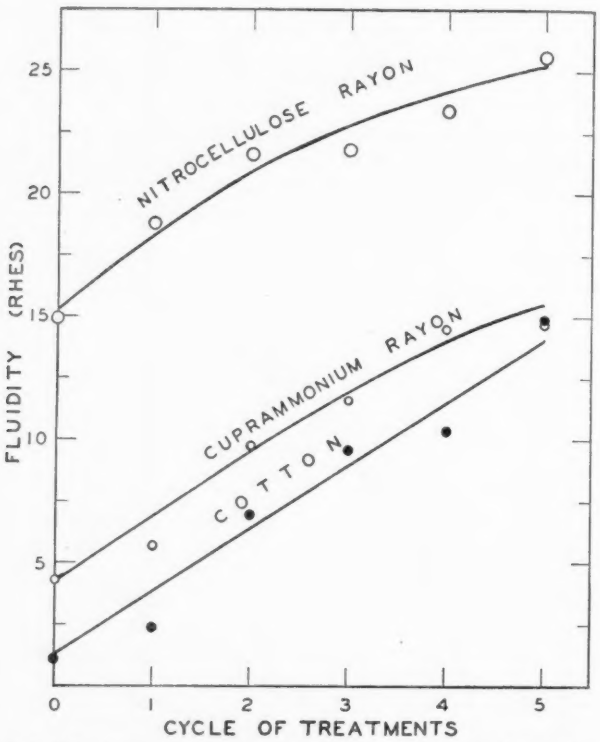

FIGURE 3.—*Fluidity in cuprammonium solution of 0.5-percent dispersions of cotton cellulose and 2-percent dispersions of regenerated cellulose rayon after repeated cycles of treatment, each consisting in an extraction with alcohol, ether, and with 1-percent solution of sodium hydroxide.*

ether is shown on the vertical axis. A continued loss in weight with successive treatments is shown for each of the three kinds of fibers. The amount of cotton dissolved in each treatment is nearly the same as is shown by the straight line that can be drawn to represent the losses. The rayons, particularly the nitrocellulose, lost rapidly in weight during the first cycle, and less rapidly thereafter.

The fluidities of dispersions of each of the three kinds of fibers in cuprammonium solution at the end of each of the cycles are shown in

[12] J. Textile Inst. **19**, T349 (1928).

figure 3. Like the loss in weight, the fluidity increased about an equal amount for each cycle of treatment. There is indication that the fluidity of the cuprammonium rayon, and particularly of the nitrocellulose rayon, is increased more rapidly in the first cycles of treatments than in the last.

Since the loss in weight and increase in fluidity of the cotton are about the same in all cycles of treatment, there does not appear to be any "optimum" time of boiling for the preparation of a "standard" cotton fiber, and there is no indication that the properties would become constant with further treatment.

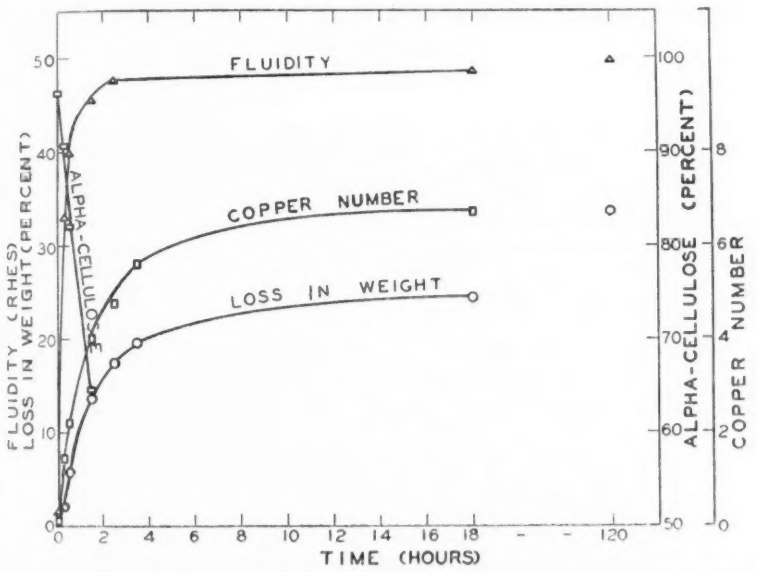

FIGURE 4.—*Changes in weight, fluidity in cuprammonium solution, copper number, and alpha-cellulose content of cotton cellulose when digested in a hydrochloric acid solution of specific gravity 1.19.*

V. DIGESTION WITH HYDROCHLORIC ACID

Ten-gram samples of cotton that had previously been subjected to one complete cycle of extractions with alcohol, ether, and dilute alkali, were placed with 250-ml portions of hydrochloric acid (sp gr 1.19) in each of seven 500-ml Pyrex glass-stoppered bottles, which were then kept at a temperature of 21° ±2° C. At intervals of ¼, ½, 1½, 2½, 3½, 18, and 120 hours, the contents of a bottle were centrifuged, the residue thoroughly washed with distilled water, dried to constant weight, and specimens tested.

The residues varied in physical form from weak fibers for the shorter periods of treatment to a powdery mass for the longer treatments. The change was first apparent in the fibers treated for 2½ hours. These fibers were brittle and could readily be reduced to a powder. The dry residues from the 18- and 120-hour treatments were tough, horny masses that were difficult to pulverize.

Figure 4 shows the effects of digestion in acid on the weight of the cotton, the fluidity of its cuprammonium solution, its copper number, and its alpha-cellulose content. A very rapid loss in weight, an increase in fluidity and in copper number, and a decrease in alpha-cellulose content occurred during the first 3½ hours. The subsequent changes took place more slowly. The products differ from those obtained with the alkali extractions in having higher copper numbers than the original fiber and much higher fluidity for the same loss in weight. They are, of course, no longer to be considered textile fibers because of the loss of fiber structure.

WASHINGTON, September 17, 1938.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1147

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FORMATION OF HYDRATED CALCIUM SILICATES AT ELEVATED TEMPERATURES AND PRESSURES

By Einar P. Flint, Howard F. McMurdie, and Lansing S. Wells

ABSTRACT

An X-ray investigation of the crystalline hydrated calcium silicates which occur naturally as minerals indicated that the following are distinct compounds: Okenite, $CaO.2SiO_2.2H_2O$; gyrolite, $2CaO.3SiO_2.2H_2O$; crestmoreite, $2CaO.2SiO_2.3H_2O$; xonotlite, $5CaO.5SiO_2.H_2O$; afwillite, $3CaO.2SiO_2.3H_2O$; foshagite, $5CaO.3SiO_2.3H_2O$; and hillebrandite, $2CaO.SiO_2.H_2O$. Riversideite is apparently not a distinct mineral and is probably the same compound as crestmoreite. Crystalline preparations having X-ray patterns identical with those of gyrolite, xonotlite, and foshagite were synthesized by hydrothermal treatment of calcium silicate in the form of the anhydrous crystalline compounds, glass, and amorphous hydrate. Other compounds formed were cristobalite, wollastonite, pseudowollastonite, $4CaO.5SiO_2.5H_2O$, $CaO.SiO_2.H_2O$, $10CaO.5SiO_2.6H_2O$, $2CaO.SiO_2.H_2O$, and $3CaO.SiO_2.2H_2O$. A low-temperature modification of anhydrous tricalcium disilicate, which inverts to the usual form at 1,024° ±5° C, resulted from the action of water vapor on tricalcium disilicate at 500° C, 380 atmospheres. Gyrolite was obtained at temperatures between 150° and 400° C, $4CaO.5SiO_2.5H_2O$ at 150° to 275°C, $CaO.SiO_2.H_2O$ at 150° C, xonotlite at 175° to 390° C, wollastonite at 400° C and higher, foshagite at 300° to 350° C, $10CaO.5SiO_2.6H_2O$ at 100° to 200° C, and $3CaO.SiO_2.2H_2O$ at 200° to 450° C. Attempts to prepare okenite, crestmoreite, afwillite, and hillebrandite were unsuccessful. Treatment of tricalcium and dicalcium silicates with water at room temperature for several years gave crystalline alteration products which were different from other known hydrated calcium silicates. That derived from dicalcium silicate had a composition approaching $3CaO.2SiO_2.1.5H_2O$. Attempts to isolate and identify the hydrated calcium silicate binding material in commercial sand-lime brick and in laboratory-prepared brick were unsuccessful, but a partial separation of the cementing material was apparently obtained. Applications of the results to the autoclave testing of cements are discussed.

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I. INTRODUCTION

The suggested application to portland cement [1] [1] of the autoclave test for soundness has renewed interest in the products of reactions between cement constituents and water at elevated temperatures and pressures. Among the possible products of such treatment are crystalline hydrated calcium silicates. Such compounds occur in nature as a group of rare but widely distributed minerals commonly found in contact zones of limestone and silicates and are evidently formed by hydrothermal processes. A number of unsuccessful attempts have been made to identify the cementing material of sand-lime brick with some of the naturally occurring calcium hydrosilicate minerals [2].

About a dozen apparently distinct varieties of these minerals are listed by J. W. Mellor [3], but several of these are based on analyses of impure specimens and inadequate optical data. For this reason it was necessary, first of all, to make a study of the natural minerals to ascertain which of these are actually distinct species. Hydrothermal syntheses of some, and determinations of the range of temperatures and pressures over which they are stable, were made. Certain difficulties were encountered. Chief among these was the slow crystallization rate of the hydrated calcium silicates, some of which apparently require months or even years to form at the lower temperatures. Consequently, the ranges of stability of the various phases have been only partially ascertained. Another difficulty lay in the close similarity in crystal habit and optical properties of most of the compounds. Confirmation by means of X-ray patterns was necessary in many cases.

II. X-RAY IDENTIFICATION OF HYDRATED CALCIUM SILICATE MINERALS

As many as possible of the hydrated calcium silicates already identified as distinctive minerals were obtained for further identification by means of X-ray diffraction patterns.[2] All were either from type localities or localities from which specimens described in the literature had been secured. Table 1 gives the name, locality, formula, and literature references accompanying the specimens of which X-ray diffraction patterns were made. Powder X-ray diffraction patterns were made also of the anhydrous calcium silicates: $3CaO.SiO_2$, β-$2CaO.SiO_2$, γ-$2CaO.SiO_2$, $3CaO.2SiO_2$, α-$CaO.SiO_2$ (artificial pseudowollastonite), and wollastonite.

[1] Figures in brackets indicate the literature references at the end of this paper.
[2] Practically all of these minerals were obtained from the United States National Museum, through the kindness of W. F. Foshag, Curator of Mineralogy.

TABLE 1.—*Hydrated calcium silicate minerals*

Name	Formula	Locality	Literature reference
Okenite	$CaO.2SiO_2.2H_2O$	Crestmore, Calif.	Eakle, Univ. Calif. Bul. Dept. Geol. **10**, 327 (1917).
Centrallasite	$4CaO.7SiO_2.5H_2O$	Wet Weather Quarry, Crestmore, Calif.	Foshag, Am. Mineral. **9**, 88 (1924).
Truscottite	$4(Ca,Mg)O.7SiO_2.5H_2O$	Benkoelen, Sumatra	Grutlerink, Verh. Geol.-Mignt. Genootschaap, Nederland, Geol. Series **8**, 197 (1925).
Gyrolite	$4CaO.6SiO_2.5(H,Na,K)_2O$	Niakornat, Greenland	Boggild, Medd. am Grönl. **34**, 93 (1908).
Crestmoreite	$2CaO.2SiO_2.3H_2O$	Crestmore, Calif.	Eakle, Univ. Calif. Bul. Dept. Geol. **10**, 327 (1917).
Riversideite	$2CaO.2SiO_2.H_2O$	Crestmore, Calif.	Eakle, Univ. Calif. Bul. Dept. Geol. **10**, 327 (1917).
Xonotlite	$5CaO.5SiO_2.H_2O$	Isle Royale, Mich.	Foshag and Larson, Am. Mineral. **7**, 23 (1922).
Afwillite	$3CaO.2SiO_2.3H_2O$	Dutoitspan Mine, Kimberly, South Africa.	Parry and Wright, Mineralog. Mag. **20**, 277-96 (1925).
Foshagite	$5CaO.3SiO_2.3H_2O$	Crestmore, Calif.	Eakle, Am. Mineral. **10**, 97 (1925).
Hillebrandite	$2CaO.SiO_2.H_2O$	Velardena District, Durango, Mexico.	Wright, Am. J. Sci. **26**, 551 (1908).

The results of this study were as follows: The minerals gyrolite, centrallasite, and truscottite, were found to be very closely related. All of the lines in the pattern of gyrolite were present in the same positions in the pattern of the truscottite sample. The truscottite sample, however, had additional lines, the more intense of which corresponded to the more intense lines of quartz. The sample of centrallasite also possessed lines common to gyrolite and truscottite as well as the more intense lines of quartz. The recorded optical properties of these minerals are also very similar; all three have the same maximum index of refraction, 1.549; all are optically negative; and gyrolite is unaxial, while centrallasite and truscottite are reported to have very small optic angles. All three of the samples studied contained perceptible amounts of isotropic material with low index of refraction occurring as microscopically thin crusts on the platy crystals or as fine laminae between the plates.

Of the hydrated monocalcium silicates, xonotlite has a pattern which is characteristic and distinctive. Some confusion has existed regarding the two minerals riversideite and crestmoreite, which possess crystallographic properties identical within experimental accuracy. Their discoverer, A. S. Eakle [4], distinguished between them by the greater water content of crestmoreite and presented a typical analysis of this mineral which corresponded to the ratios $1.09CaO:1.00SiO_2:1.27H_2O$, after correcting for the P_2O_5, SO_3, and CO_2 present. Similarly, the analysis given for riversideite conformed to the ratios $1.01CaO:1.00SiO_2:0.62H_2O$. The analyses showed that both minerals had the same impurities in comparable amounts.

In order to determine the significance of these reported differences in water content, some experiments were made on a sample of crestmoreite obtained from the United States National Museum. The loss on ignition to a temperature of 1,100° C was 13.09 percent. After heating the crestmoreite at 110° C for 3 hours, the loss on ignition (H_2O+CO_2) was reduced to 9.80 percent, which is only slightly higher than the water content of 8.11 percent reported for riversideite. The indices and appearance of the crystals were unchanged and the distinctive X-ray pattern of the original mineral was not altered, which indicated that the water was not constitutional.

Another characteristic of riversideite, according to Eakle, was its occurrence in narrow seams in mounds of vesuvianite, whereas crestmoreite was associated with calcite. However, a sample labelled "riversideite," from Ward's Natural Science Establishment, in which the hydrated calcium silicate appeared as narrow veins in lumps of vesuvianite, was found by its X-ray pattern to be identical with crestmoreite from the United States National Museum. Thus, crestmoreite may occur associated with the same mineral as was reported for riversideite.

A sample labelled "riversideite" from the United States National Museum showed complete identity of pattern with foshagite from the Museum. The identical X-ray diffraction pattern of a preparation obtained by treating $5CaO{\cdot}3SiO_2$ glass with water (as will be described later) indicates that both are foshagite.

Because no sample of riversideite could be obtained which was distinct from other minerals, and, in view of the fact that none of its reported properties are characteristic it is believed that riversideite does not exist as an independent compound.

A sample labelled "foshagite" from the Wet Weather Quarry, Crestmore, Calif., obtained from Ward's Natural Science Establishment, was found to be made up of two minerals. One gave an X-ray pattern identical with that of foshagite; the other was identical with that of hillebrandite from the Velardena Mines, Mexico—both samples were obtained from the United States National Museum. This may account for the fact that Vigfusson [5] found the X-ray patterns of foshagite and hillebrandite identical and concluded that they were the same mineral. The remaining minerals, okenite, afwillite, and hillebrandite, gave characteristic and distinctive X-ray patterns.

A sample of an unknown hydrated calcium silicate mineral obtained from the United States National Museum proved to be distinctive in X-ray pattern and optical properties. Analysis gave the following composition: 35.57 percent of CaO, 0.30 percent of MgO, 1.19 percent of R_2O_3, 42.7 percent of SiO_2, 19.76-percent ignition loss; total 99.61 percent. The amount of sample available was insufficient for a CO_2 determination, but petrographic examination indicated that the amount of carbonate present was probably less than 5 percent. Assuming the ignition loss to represent the water content, the analysis conforms to $0.89CaO:1.00SiO_2:1.54H_2O$, which does not correspond very closely to any simple CaO/SiO_2 ratio. The sample consisted of aggregates of fibrous crystals having parallel extinction, positive elongation, and indices of refraction [3] $\alpha=1.540 \pm 0.003$, $\gamma=1.548 \pm 0.003$. Some finely divided material as well as glassy isotropic impurity was present.

III. HYDROTHERMAL SYNTHESIS OF HYDRATED CALCIUM SILICATES

1. MATERIALS

The starting materials were precipitated hydrated calcium silicate, calcium silicate glass, and the crystalline anhydrous calcium silicates.

A previous investigation [6] had shown that solutions containing

[3] In this paper α and γ are used to indicate the minimum and maximum refractive indices, respectively, although, in some cases, it is not certain that the crystals are biaxial.

0.5 g SiO_2/l and about 0.05 g CaO/l can be prepared by boiling purified silica gel with dilute lime solution for several days. By adding saturated limewater to such a solution in varying proportions, hydrated calcium silicate precipitates were prepared having CaO/SiO_2 molar ratios ranging from 0.1 to 1.5. The precipitates were washed with alcohol and ether, dried in a desiccator over calcium chloride, and analyzed to determine their CaO/SiO_2 molar ratios. These preparations are designated in the tables by the letters "aq" to indicate their indefinite water content.

The calcium silicate glasses were prepared by quenching charges of the proper compositions wrapped in platinum foil from temperatures above the liquidus. Small amounts of boric oxide were added to some of these charges to bring the temperature of complete melting within the range of the furnace.

The anhydrous calcium silicates were laboratory preparations of high purity.

2. APPARATUS AND EXPERIMENTAL PROCEDURE

Four bombs were used in this investigation, three of which were constructed according to designs of the Geophysical Laboratory [7]. Two of these bombs are of stainless steel and of 40-ml capacity, and one is of tool steel and of 18-ml capacity. These bombs were heated in insulated Nichrome-wire furnaces having heating zones twice as long as the bombs. By means of modified bimetallic regulators, each furnace could be maintained at temperatures between 150° and 600° C within ± 5°C for long periods of time.

Temperatures were measured by means of Chromel-Alumel thermocouples in conjunction with a portable potentiometer. The thermocouples were inserted in wells drilled in the bombs.

The calcium silicate starting materials were inclosed in platinum capsules of 3-ml capacity and placed with water in the bombs in such a way that the solid was in contact with the liquid at temperatures below the critical point of water. Sufficient water was always used so that the liquid phase was present up to the critical point (374° C, 218 atm.). The pressures below 374° C are therefore those of saturated steam in contact with liquid water; those above 374° C were read from the the curves of van Nieuwenburg and Blumendal [8], knowing the mass of water inserted and the volume of the bomb.

After completion of the heating period, the bomb was removed from its furnace and cooled by immersion in water; the product was then removed, washed with alcohol and ether, and dried in a desiccator over a mixture of calcium chloride and soda-lime or Dehydrite. Petrographic examinations, and, in some cases, chemical analyses were made on the products. X-ray diffraction patterns were taken of most of the preparations for comparison with those of the natural minerals.

The fourth bomb is of 2-liter capacity, is made of tool steel, and was used up to 225° C. As figure 1 shows, it was so designed that the liquid and solid phases could be quickly separated without opening the bomb. In use the bomb was first inverted and the materials were placed in the compartment designed as upper chamber in the figure. The bomb in this position was placed in a heating oven equipped with a fan. On completion of the heating period, the bomb

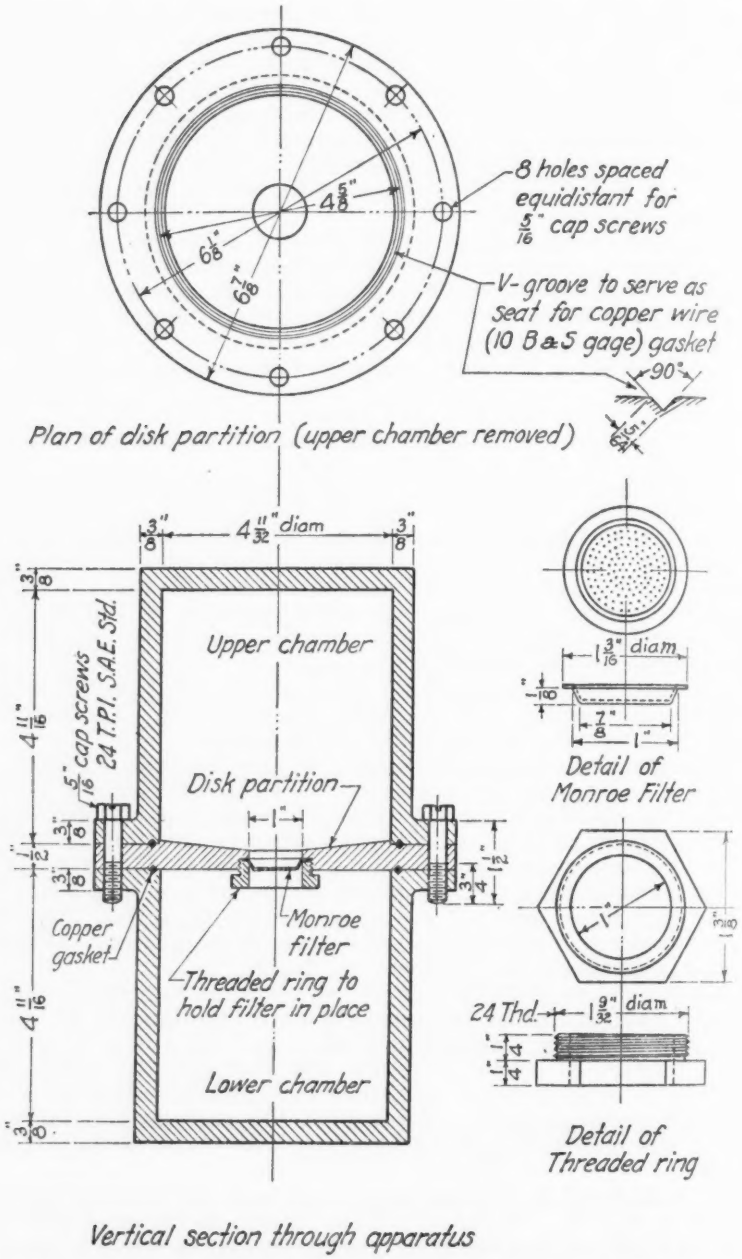

FIGURE 1.—*Bomb for hydrothermal synthesis (in position for filtering).*

was turned over and the lower chamber (fig. 1) placed in cold water. Condensation of steam in this chilled compartment forced the liquid through a Munroe platinum filter in the middle disk.

3. PRELIMINARY EXPERIMENTS

At a given temperature and pressure the composition of the product will depend not only on the composition of the starting material, but also on the relative solubilities of lime and silica in the liquid. The CaO/SiO_2 ratio of the product may be either raised or lowered, depending upon whether lime or silica has the greater concentration in the solution formed.

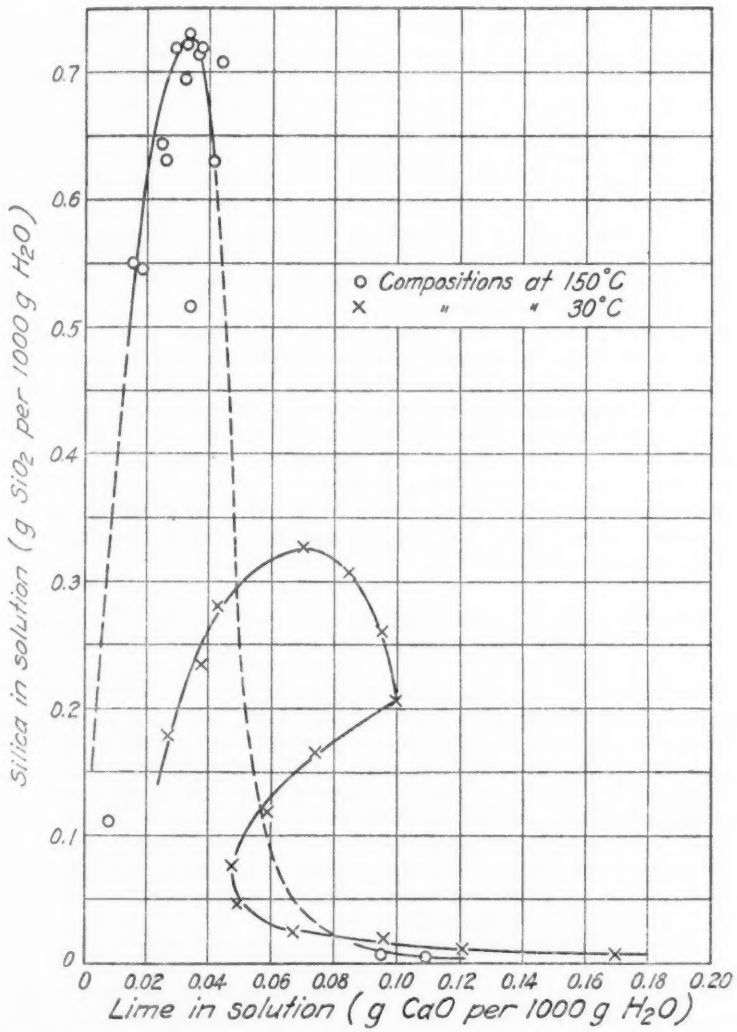

FIGURE 2.—*Solubilities of silica in lime solutions at 30° and 150° C.*

To obtain some information on this factor, a number of determinations were made of the solubility of amorphous silica in solutions of calcium hydroxide at 150° C. Silica gel in amounts between 1 and

10 g was treated with 700 ml of lime solution of various concentrations in the large bomb for 5 days with occasional shaking. The resulting solutions, which remained clear for a short time after cooling, were analyzed for lime and silica, and the results are shown in figure 2. The maximum silica concentration was 0.73 g/1,000 g of H_2O at 0.033 g of CaO/1,000 g of H_2O, and the silica content of the solutions decreased rapidly when the lime content either exceeded or fell below this value. The lower curve in figure 2 represents the solubility relations found at 30° C in a previous investigation [6]. In neither curve do the values represent the solubilities of any one of the crystalline forms of silica, but they were nevertheless fairly reproducible and to some extent indicative of the solubilities of the materials used in these experiments.

Several determinations were made also of the solubility of calcium hydroxide in the temperature range 100° to 200° C. The solubility at 100° C was found to be less than half the solubility at room temperature, or approximately 0.5 g of CaO/1,000 g of H_2O, and the solubilities at 150° and 200° C are approximately 0.25 and 0.1 g of CaO/1,000 g of H_2O, respectively.

In the case of experiments in the three small bombs, where 0.5-gram quantities of solid were treated with usually not more than 10 ml of water, the results indicate that the CaO/SiO_2 molar ratio of the product cannot be much different from that in the starting material. In some experiments in the large bomb, however, where a large excess of water was used, the molar ratio of the product may be considerably different from that of the starting material.

It is evident that the limited solubilities of lime and silica and their compounds would make a complete investigation of the liquid phase in this system very difficult.

4. HYDROTHERMAL TREATMENT OF CALCIUM SILICATES OF VARYING MOLAR RATIOS OF LIME TO SILICA

The effect of hydrothermal treatment on calcium silicates of CaO/SiO_2 molar ratios varying from 0.1 to 4.0 will be described in the following sections. For convenience, the various compositions are divided into groups of the same CaO/SiO_2 ratio or having a limited range of molar ratios. The lengths of time required for complete crystallization to occur varied with the different molar ratios and the periods listed are somewhat arbitrary. In general, however, the times of heating represent those necessary to form a well-crystallized sample as determined by preliminary experiments.

(a) MOLAR RATIO CaO/SiO_2 VARYING FROM 1:10 TO 1:2

The least basic of the known calcium hydrosilicates is the mineral okenite, $CaO.2SiO_2.2H_2O$. The results of treating calcium silicates having the molar ratio of okenite, as well as those of lower molar ratios are described in table 2.

TABLE 2.—*Results of experiments on compositions varying in molar ratio* CaO/SiO_2 *from 1:10 to 1:2*

Experiment number	Starting material	Temperature	Pressure	Time	Product
		°C	*atm*	*Days*	
1	0.1CaO:SiO_2:aq [1]	390	261	14	Cristobalite+xonotlite.
2	.2CaO:SiO_2:aq	450	420	12	Cristobalite+?
3	.3CaO:SiO_2:aq	200	15	50	$4CaO.5SiO_2.5H_2O$+?
4	.5CaO:SiO_2 glass [2]	150	5	58	Cristobalite+glass.
5	do	225	25	21	Gyrolite+glass.
6	do	300	85	21	Do.
7	do	400	290	7	Do.
8	do	450	300	13	Pseudowollastonite+?

[1] "Aq" here and in following tables designates the indefinite water content of the amorphous calcium silicate precipitates.
[2] Contained 3 percent of B_2O_3.

The crystallization of cristobalite and psuedowollastonite at temperatures far removed from those at which they crystallize from anhydrous melts is of some interest. The cristobalite crystals were very small but good X-ray patterns were obtained. Other investigators have obtained cristobalite by hydrothermal treatment at corresponding temperatures, but usually from neutral or acidic solutions [9]. Xonotlite, $5CaO.5SiO_2.H_2O$, which crystallized with cristobalite in experiment 1, occurred in fairly large, well-formed crystals. Later experiments indicated that xonotlite crystallizes comparatively rapidly at 390° C, which may account for its formation here in preference to less basic hydrosilicates.

In experiment 3 the formation of the compound $4CaO.5SiO_2.5H_2O$, the synthesis of which will be discussed in a later section, cannot be accounted for. The formation of okenite or of gyrolite was more to be expected under these conditions.

The pseudowollastonite obtained in experiment 8 crystallized in aggregates of fibrous needles of parallel extinction and negative elongation. The X-ray pattern was identical with that of α-$CaO.SiO_2$.

The product in experiments 5, 6, and 7 gave the X-ray pattern of gyrolite. In the best crystallized of these preparations, No. 6, the product had the appearance of aggregates of parallel fibers. The ignition loss of this preparation, however, was only 4.8 percent as compared with a theoretical water content for $4CaO.6SiO_2.4H_2O$ of 10.97 percent, or for $4CaO.7SiO_2.5H_2O$ of 12.26 percent, which indicated that conversion was incomplete.

Attempts to obtain the mineral okenite were unsuccessful. A product which the authors suggested might be okenite was synthesized by Schlaepfer and Niggli [10] by treatment of mixtures of SiO_2, CaO, Al_2O_3, and KOH with water at 470° C. They reported similarities in appearance and mean index to the natural mineral. These criteria would seem to be insufficient in view of the fact that some of the other hydrated calcium silicates have almost the same index and crystal habit.

(b) MOLAR RATIO CaO/SiO_2 VARYING FROM 4:7 TO 2:3

The CaO/SiO_2 molar ratio 0.59 corresponds to the reported ratio of the minerals centrallasite and truscottite, and the ratio 0.66 corresponds to that of the mineral gyrolite. Results of treatment of such compositions are given in table 3.

TABLE 3.—*Results of experiments on compositions varying in molar ratio* CaO/SiO_2 *from 4:7 to 2:3*

Experiment number	Starting material [1]	Temperature	Pressure	Time	Product
		°C	atm	Days	
9	0.59CaO:SiO_2:aq	150	5	42	Gyrolite.
10	do	225	25	28	Do.
11	do	250	39	35	Gyrolite+xonotlite.
12	do	300	85	14	Gyrolite.
13	0.59CaO:SiO_2 glass	300	85	37	Do.
14	do	350	163	6	Do.
15	do	450	300	6	Pseudowollastonite+?.
16	0.66CaO:SiO_2:aq	250	39	40	Gyrolite.
17	0.66CaO:SiO_2 glass	300	85	35	Do.
18	do	500	380	14	Pseudowollastonite+?.

[1] The glasses contained no B_2O_3.

The gyrolite crystals occurred as bundles of parallel fibers with positive elongation, parallel extinction, uniaxial negative, and indices of refraction $\epsilon=1.536$, $\omega=1.548$. A photomicrograph of the preparation from experiment 16 is shown in figure 3. Figure 4 shows preparation 11, which in some portions contained large broom-shaped aggregates of xonotlite surrounded by gyrolite.

A chemical analysis of preparation 10, initial molar ratio 0.59, gave the composition: 34.18 percent of CaO, 55.96 percent of SiO_2, 9.86 percent of H_2O, corresponding to the ratios: $1.96CaO:3.00SiO_2:1.76H_2O$. An analysis of the best preparation, No. 16, initial molar ratio 0.66, gave the composition: 33.58 percent of CaO, 0.36 percent of R_2O_3,[4] 54.02 percent of SiO_2, 11.40 percent of H_2O; corresponding to the ratios: $2.00CaO:3.00SiO_2:2.11H_2O$. These analyses justify assigning to gyrolite the formula $2CaO.3SiO_2.2H_2O$. The fact that the CaO/SiO_2 molar ratio of 0.59 was unstable and increased to 0.65 in experiment 10, while a ratio of 0.66 remained unchanged in experiment 16, indicates that 0.66 is the stable ratio. In conjunction with the X-ray data, this evidence confirms the belief that centrallasite and truscottite are not distinct minerals but are rather impure forms of gyrolite.

The synthesis of gyrolite was claimed by E. Baur [11] from a mixture of SiO_2, Al_2O_3, KOH, and CaO treated with water at 450° C. The optical properties which he reported for his product were, however, not those of gyrolite. No other report on the synthesis of gyrolite was found in the literature.

(c) MOLAR RATIO CaO/SiO_2, 4:5

The results of these experiments are listed in table 4.

TABLE 4.—*Results of experiments on compositions varying in molar ratio* CaO/SiO_2, 4:5

Experiment number	Starting material	Temperature	Pressure	Time	Product
		°C	atm	Days	
19	0.80CaO:SiO_2:aq	150	5	42	$4CaO.5SiO_2.5H_2O$.
20	do	225	25	14	Do.
21	do	250	39	7	Do.
22	0.76CaO:SiO_2:aq	275	59	21	Do.
23	0.80CaO:SiO_2:aq	300	85	14	Xonotlite.
24	do	350	163	10	Do.
25	do	500	380	7	Wollastonite.

[4] The small percentages of R_2O_3 in the products of hydrothermal synthesis reported here and elsewhere in this paper are largely Fe_2O_3 as a contamination from the iron of the bomb.

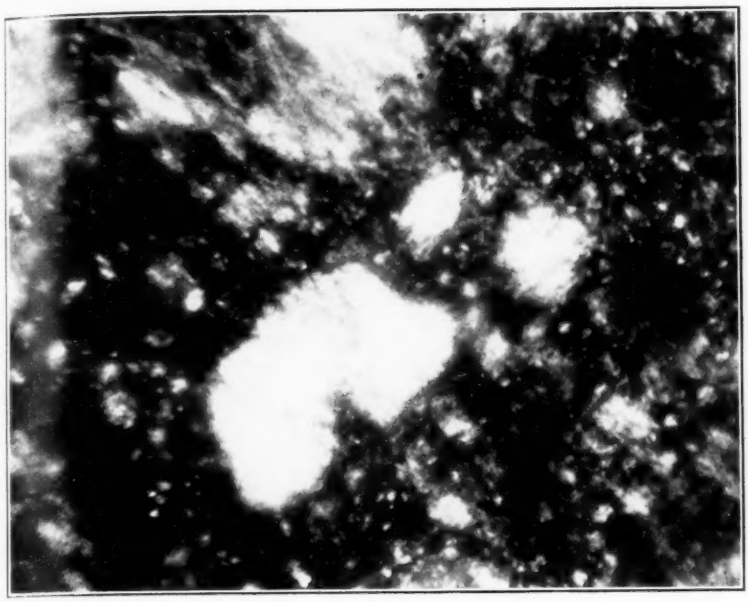

FIGURE 3.—*Synthetic gyrolite.*
Crossed nicols, magnification ×180

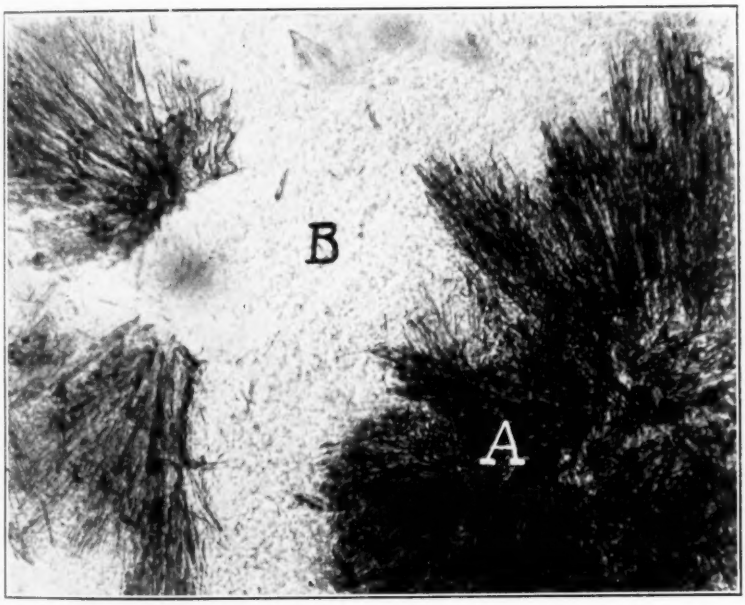

FIGURE 4.—*Synthetic (A) xonotlite + (B) gyrolite.*
Magnification ×180.

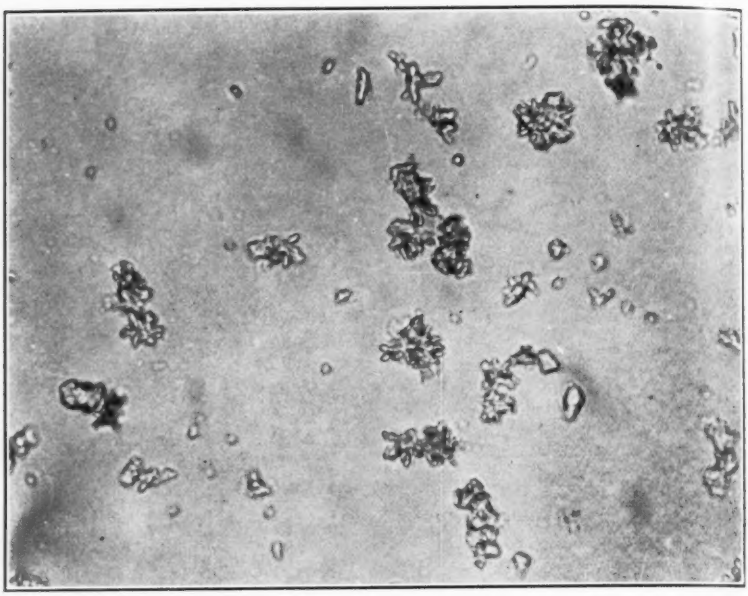

FIGURE 5.—*Synthetic* $CaO.SiO_2.H_2O$.
Magnification ×900.

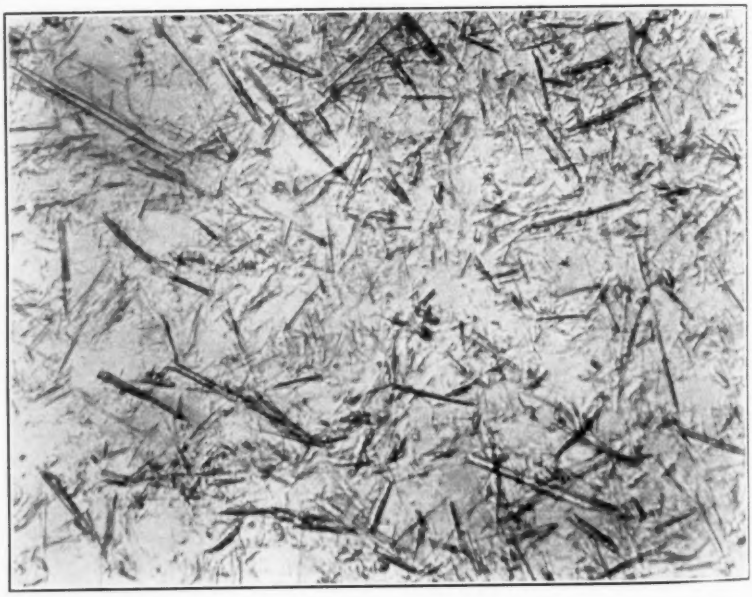

FIGURE 6.—*Synthetic xonotlite.*
Magnification ×180.

The product of experiments 19, 20, and 21 consisted of very small needles of moderate birefringence and mean refractive index 1.54, positive elongation and parallel extinction. The X-ray pattern of this phase is distinctive. Analysis of preparations 19 and 21 gave the following results:

Components	Preparation 19	Preparation 21
	Percent	*Percent*
CaO	36.86	38.96
R_2O_3	0.37	
SiO_2	47.84	48.71
H_2O	14.44	11.84
Total	99.51	99.51

corresponding to the ratios $4.13CaO:5.00SiO_2:5.03H_2O$ in the case of preparation 19 and to $4.00CaO:5.00SiO_2:4.15H_2O$ for preparation 21. The ignition loss of preparation 20 was 13.97 percent, corresponding to $4CaO:5SiO_2:4.7H_2O$. The formula of this compound is therefore tentatively placed at $4CaO.5SiO_2.5H_2O$.

The mineral most similar to this preparation is tobermorite discovered by M. F. Heddle [12], who assigned to it the formula $3(4CaO.5SiO_2.H_2O).10H_2O$, or $4CaO.5SiO_2.4\frac{1}{3}H_2O$. P. Groth [13] suggested the formula $4CaO.5SiO_2.4H_2O$. Unfortunately, Heddle was unable to determine the crystalline form of the mineral and lists none of its optical properties, so no further comparison with the synthetic product is possible.

(d) MOLAR RATIO CaO/SiO_2, 1:1

The hydrated monocalcium silicate minerals are crestmoreite, $2CaO.2SiO_2.3H_2O$; and xonotlite, $5CaO.5SiO_2.H_2O$. Experiments on starting materials of this ratio are listed in table 5.

Experiments 26 and 40 involved pseudowollastonite, which underwent no transformation in 6 weeks at 150° C, but it was 50 percent transformed to wollastonite in 3 weeks at 500° C, 480 atmospheres.

TABLE 5.—*Results of experiments on* $1CaO:1SiO_2$ *compositions*

Experiment number	Starting material	Temperature	Pressure	Time	Product
		°C	*atm*	*Days*	
26	Pseudowollastonite	150	5	42	Unchanged.
27	0.95CaO:SiO_2:aq	150	5	42	Amorphous.
28	1.04CaO:SiO_2:aq	150	5	60	$CaO.SiO_2.H_2O$.
29	do	175	9	79	Xonotlite.
30	do	200	15	73	Do.
31	1.0CaO:SiO_2 glass [1]	250	39	10	Do.
32	1.04CaO:SiO_2:aq	320	109	7	Do.
33	do	370	207	4	Do.
34	do	380	225	4	Do.
35	do	390	225	4	Do.
36	Xonotlite	390	169	7	Do.
37	do	390	72	4	Do.
38	1.04CaO:SiO_2:aq	400	290	5	Wollastonite.
39	do	450	300	5	Do.
40	Pseudowollastonite	500	480	21	50 percent of wollastonite+50 percent of pseudowollastonite.

[1] Contained no B_2O_3.

Amorphous monocalcium silicate hydrate treated with water at 150° C for 6 weeks remained amorphous, but a sample treated for 60 days at the same temperature (experiment 28) crystallized to a single phase of the following composition: 41.97 percent of CaO, 43.97 percent of SiO_2, 14.47 percent of H_2O corresponding to the ratios: $1.02CaO:1.00SiO_2:1.10H_2O$, or a monohydrate of monocalcium silicate. The preparation was rather finely divided, but under the oil-immersion objective it appeared to be composed of thick needle- and lath-shaped crystals with parallel extinction, negative elongation, mean index 1.603. The X-ray pattern was distinctive and different from that of crestmoreite. A photomicrograph of these crystals is shown in figure 5.

Monocalcium silicate hydrate treated with water between 175 and 390° C for a sufficient time crystallized completely to a product having the optical properties and X-ray pattern of xonotlite, $5CaO.5SiO_2.H_2O$. A typical analysis is that of the preparation from experiment 33 which was: 46.15 percent of CaO, 50.10 percent of SiO_2, 3.35 percent of H_2O, corresponding to the ratios: $0.99CaO:1.00SiO_2:0.22H_2O$. A photomicrograph of these crystals is shown in figure 6. They are fibrous needles of parallel extinction, positive elongation, having indices of refraction: $\alpha=1.583\pm0.003$, $\gamma=1.594\pm0.003$.

Crystallization of xonotlite occurred most rapidly between 320° and 390° C, in which range it was complete in 4 to 7 days.

Experiments 37 and 38 fix the upper temperature limit at which xonotlite is stable at 395° ±10° C. Xonotlite remained the stable phase at 390° C, on reduction of the pressure from 225 to 72 atmospheres. Above this temperature complete crystallization to large well-formed laths of wollastonite occurred in heating periods of 5 days. A photomicrograph of these crystals is shown in figure 7.

Nieuwenburg and Blumendal [14] reported having obtained wollastonite by steaming a lime-silica mixture out of contact with the liquid for 2 days at 365° C. Their experiment was repeated by steaming monocalcium silicate hydrate out of contact with the liquid at 365° C for 3 days. The product was xonotlite.

Nagai [15] and Kohler [16] reported having synthesized xonotlite, but neither of these authors gives any confirmatory optical or X-ray data.

(e) MOLAR RATIO CaO/SiO_2, 3:2

The mineral afwillite, $3CaO.2SiO_2.3H_2O$, possesses the CaO/SiO_2 molar ratio used in experiments 41 to 49, inclusive, table 6.

TABLE 6.—*Results of experiments on* $3CaO:2SiO_2$ *compositions*

Experiment number	Starting material	Temperature	Pressure	Time	Product
		°C	atm	Days	
41	α-$3CaO.2SiO_2$	150	5	42	>50 percent unaltered.
42	$1.53CaO:SiO_2$:aq	150	5	70	$CaO.SiO_2.H_2O$+?
43	do	200	15	73	Do.
44	α-$3CaO.2SiO_2$ (prep. 41)	250	39	10	?
45	$1.44CaO:SiO_2$:aq	250	39	14	Xonotlite+?
46	$1.42CaO:SiO_2$:aq	300	85	14	Do.
47	$1.45CaO:SiO_2$:aq	350	163	14	Do.
48	$1.53CaO:SiO_2$:aq	400	270	5	Do.
49	α-$3CaO.2SiO_2$	500	380	14	β.$3CaO.2SiO_2$.

FIGURE 7.—*Synthetic wollastonite.*
Magnification ×180.

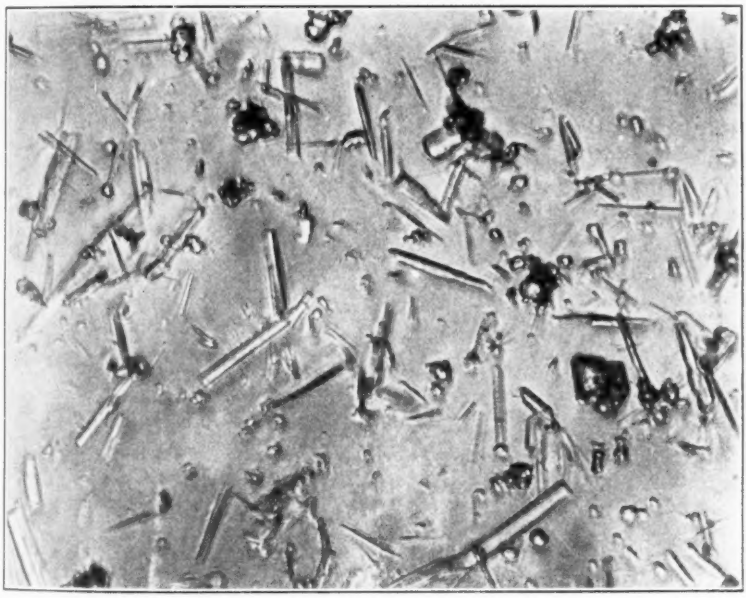

FIGURE 8.—*β-tricalcium disilicate.*
Magnification ×900.

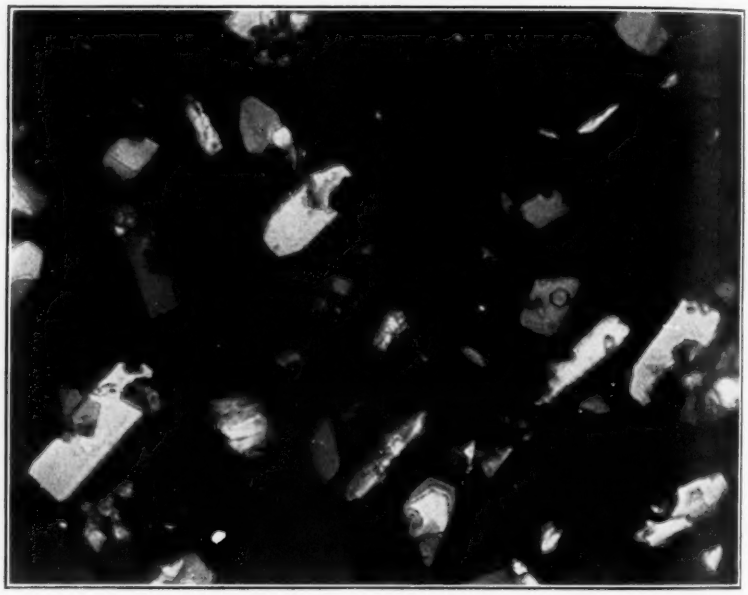

FIGURE 9.—*Synthetic* $10CaO.5SiO_2.6H_2O$.
Crossed nicols, magnification ×400.

In experiment 41 more than 50 percent of the anhydrous tricalcium disilicate, treated with water at 150° C for 6 weeks, remained unaltered. The alteration product consisted of irregular masses of low-birefringent material of refractive index 1.57, and was not identified. This material kept an additional 10 days at 250° C (experiment 44) was largely altered to low-birefringent aggregates of mean refractive index, 1.62+. The X-ray pattern was different from that of afwillite and could not be identified.

Treatment of anhydrous tricalcium disilicate with water at 500° C, 380 atmospheres, for 2 weeks (experiment 49) resulted in 90-percent conversion to a new phase. Inasmuch as the tricalcium disilicate contained a few percent of impurities (mostly dicalcium silicate) there were also present some alteration products of the impurities, including some dicalcium silicate hydrates, the hydrothermal formation of which will be described subsequently. The new phase consisted of small needle- and lath-shaped crystals of parallel extinction and positive elongation. The indices of refraction are: $\alpha=1.608 \pm 0.003$, $\gamma=1.615 \pm 0.003$. A photomicrograph of these crystals is shown in figure 8.

Determinations of ignition loss showed the new compound to be anhydrous. Its X-ray pattern proved to be different from that of ordinary tricalcium disilicate or any of the other anhydrous calcium silicates. Ignition for a few minutes over a Méker burner converted it back to the usual form of tricalcium disilicate.

The evidence indicated that the new phase was a low-temperature form of tricalcium disilicate. This was confirmed by experiments using the quenching method. A sample held overnight at 1,020° C gave an unchanged X-ray pattern, while a sample held at 1,027° C overnight gave the pattern of ordinary tricalcium disilicate. The inversion of the low-temperature form of tricalcium disilicate to the high-temperature form is therefore placed at 1,024°C ±5° C.

Attempts to prepare the mineral afwillite were unsuccessful. Amorphous hydrates having the CaO/SiO_2 molar ratio of this compound when heated at temperatures of 150° and 200° C in the presence of water crystallized largely to $CaO.SiO_2.H_2O$, and at temperatures ranging from 250° to 400° C crystallized largely to xonotlite. The secondary phases could not be distinguished petrographically or by the X-ray patterns. Raising the CaO/SiO_2 molar ratio has the effect of making both $CaO.SiO_2.H_2O$ and xonotlite stable at higher temperatures than was the case with the preparations of pure hydrated monocalcium silicate.

(f) MOLAR RATIO CaO/SiO_2, 5:3

The compositions treated in the experiments reported in table 7 corresponded in lime-silica ratio to the mineral foshagite, $5CaO.3SiO_2.3H_2O$.

TABLE 7.—*Results of experiments on* $5CaO:3SiO_2$ *compositions*

Experiment number	Starting material	Temperature	Pressure	Time	Product
		°C	atm	Days	
50	1.67CaO:SiO_2 glass [1]	200	15	73	?
51	do	300	85	53	Foshagite+glass.
52	do	350	163	17	Foshagite+glass.

[1] Contained 7 percent of B_2O_3.

The product of experiment 50 had the same X-ray pattern as that of the product obtained by treating anhydrous dicalcium silicate and dicalcium silicate glass with water at relatively low temperatures, and will be discussed in the next section.

The product of experiments 51 and 52 was a low-birefringent material without definite crystalline form and of mean index of refraction 1.595, which checks well with the mean index of foshagite. The X-ray patterns showed complete correspondence with the X-ray pattern of foshagite obtained from the United States National Museum. Conversion of the glass to the hydrate was not complete even in experiment 51, as the product gave an ignition loss of only 5.7 percent, compared with a theoretical loss for foshagite of 10.5 percent.

A sample of amorphous hydrate of CaO/SiO_2 molar ratio 1.68 steamed at 300° C out of contact with water gave a product having the X-ray pattern of $CaO.SiO_2.H_2O$. The manner of combination of the excess lime could not be determined.

(g) MOLAR RATIO CaO/SiO_2, 2:1

Results of experiments on compositions having a dicalcium silicate molar ratio, to which the mineral hillebrandite, $2CaO.SiO_2.H_2O$, corresponds, are listed in table 8.

TABLE 8.—*Results of experiments on* $2CaO:1SiO_2$ *compositions*

Experiment number	Starting material	Temperature	Pressure	Time	Product
		°C	atm		
53	β-$2CaO.SiO_2$	25	1	10 years	?
54	do	100	1	9 days	$10CaO.5SiO_2.6H_2O$+β-$2CaO.SiO_2$.
55	γ-$2CaO.SiO_2$	150	5	4 days	$10CaO.5SiO_2.6H_2O$+γ-$2CaO.SiO_2$.
56	β-$2CaO.SiO_2$	150	5	1 day	Scarce $10CaO.5SiO_2.6H_2O$ +β-$2CaO.SiO_2$.
57	do	150	5	7 days	Pure $10CaO.5SiO_2.6H_2O$.
58	$2CaO:SiO_2$ gel	150	5	10 days	95% of $10CaO.5SiO_2.6H_2O$.
59	$2CaO:SiO_2$ glass (12% of B_2O_3)	150	5	23 days	Same as preparation 53.
60	90% of γ-$2CaO.SiO_2$+10% of natural hillebrandite.	150	5	14 days	$10CaO.5SiO_2.6H_2O$+natural hillebrandite.
61	Preparation 53	175	9	41 days	Same product as preparation 53.
62	β-$2CaO.SiO_2$	200	15	3 days	$10CaO.5SiO_2.6H_2O$.
63	$2CaO:SiO_2$ gel	225	25	44 days	$2CaO.SiO_2.H_2O$.
64	$3CaO:2SiO_2$:aq+CaO	225	25	47 days	$CaO.SiO_2.H_2O$+?.
65	β-$2CaO.SiO_2$	250	39	15 days	$2CaO.SiO_2$ aq.
66	$10CaO.5SiO_2.6H_2O$	250	39	14 days	$10CaO.5SiO_2.6H_2O$.
67	90% of γ-$2CaO.SiO_2$+10% of natural hillebrandite.	250	39	14 days	Natural hillebrandite+$2CaO.SiO_2$aq.
68	$3CaO:2SiO_2$:aq+CaO	300	85	7 days	$CaO.SiO_2.H_2O$+?.
69	do	350	163	8 days	$CaO.SiO_2.H_2O$+$3CaO.SiO_2.2H_2O$.
70	$10CaO.5SiO_2.6H_2O$	450	400	7 days	$2CaO.SiO_2.2/3H_2O$.

Five g of β-dicalcium silicate treated with 500 ml of water for 10 years at room temperature (experiment 53) and shaken at intervals gave a product having a distinctive X-ray pattern and possessing a composition corresponding to the ratios $1.8CaO:1.0SiO_2:2.1H_2O$. It contained about 5 percent of calcite with the bulk of the material consisting of weakly birefringent masses without definite crystalline form. In order to effect further crystallization this material was

heated in the presence of water for 6 weeks at a temperature of 175° C (experiment 61). It was then completely crystallized to very fine needles of low birefringence and mean index of refraction 1.60. A chemical analysis gave the composition: 52.94 percent of CaO, 0.78 percent of R_2O_3, 36.50 percent of SiO_2, 9.69 percent of H_2O, which corresponds to the molar ratios: $1.55CaO:1.00SiO_2:0.88H_2O$. Allowing for the calcite which the sample contained, this analysis agrees fairly well with the formula $3CaO.2SiO_2.1.5H_2O$. The pattern is not like that of afwillite. The same X-ray pattern was given by dicalcium silicate glass (containing 12 percent of B_2O_3) treated with water at 150° C for 3 weeks (experiment 59) and also by $5CaO.3SiO_2$ glass (containing 7 percent of B_2O_3) at 200° C for 10 weeks (experiment 50, table 7).

Treating dicalcium silicate with water between 100° and 200° C usually produces an orthorhombic hydrate of dicalcium silicate. This compound is identical with crystals found by Thorvaldson and Shelton [17] in steam-cured portland cement and prepared in a pure state by Vigfusson, Bates, and Thorvaldson [18]. Reference to the preparation of the same compound from mixtures of lime, silica, and water and from tricalcium silicate and water has also been made by Flint and Wells [6]. The crystals are extremely thin (rarely more than 3 microns in thickness), lath-like plates often occurring as simple rectangular parallelopipeds but not infrequently with domatic faces bevelling the prismatic forms. The measured indices of refraction agree with those fixed by previous investigators: $\alpha=1.614\pm0.002$, $\beta=1.620\pm0.002$, $\gamma=1.633\pm0.002$. The crystals are biaxial positive. There is a perfect cleavage normal to the elongation. A photomicrograph is shown in figure 9.

Analysis of a typical preparation gave the composition: 56.64 percent of CaO, 0.46 percent of R_2O_3, 31.14 percent of SiO_2, and 11.34 percent of H_2O, corresponding to the ratios: $1.96CaO:1.00SiO_2:1.19H_2O$. Prolonged heating in an oven maintained at a temperature of 110° C reduced the water content to 10.90 percent, which corresponds to a H_2O/SiO_2 molar ratio of 1.17. Analysis of several other preparations also gave water contents corresponding closely to $1.2H_2O:1.0SiO_2$. The average of three analyses of this compound presented by Vigfusson, Bates, and Thorvaldson [18] likewise gave a H_2O/SiO_2 molar ratio of 1.24. It, therefore, appears probable that the water in excess of 1 mole is constitutional, and accordingly, the formula $10CaO.5SiO_2.6H_2O$ is suggested for the compound.

As shown in table 8, $10CaO.5SiO_2.6H_2O$ resulted from treatment with water of β- and γ-dicalcium silicates and $2CaO:1SiO_2$ mixtures of calcium oxide and silica gel. At 100° C (experiment 54), 9 days' boiling of 1 g of β-dicalcium silicate with 25 ml of water under a reflux gave about 30-percent conversion to $10CaO.5SiO_2.6H_2O$. Well-formed crystals of $10CaO.5SiO_2.6H_2O$ were also obtained by treatment of portland cement clinkers with water at 100° and 175° C. A photomicrograph of the product obtained at 175° C is given in figure 10.

Attempts to prepare hillebrandite by treating mixtures of natural hillebrandite and dicalcium silicate with water at 150° and 200° C (experiments 60 and 67) were unsuccessful. The results obtained by Kohler [16], who reported having prepared hillebrandite by heating a mixture of β-dicalcium silicate and water at temperatures ranging from 200° to 290° C, could not be duplicated. The synthesis of hille-

brandite from mixtures of CaO and amorphous SiO_2 in the presence of $CaCl_2$ heated with water at 470° C has been claimed by Schlaepfer and Niggli [10].

Treatment of $10CaO.5SiO_2.6H_2O$ at 250° C for 2 weeks (experiment 66) produced no change; treatment at 450° C, 400 atmospheres, for 1 week gave a product of unchanged crystal form but having the indices of refraction: $\alpha=1.642$, $\gamma=1.672$, which are about 0.03 higher than the corresponding indices of $10CaO.5SiO_2.6H_2O$. This material gave a distinctive X-ray pattern and its composition corresponded to the formula, $6CaO.3SiO_2.2H_2O$.

In experiment 65, β-dicalcium silicate heated in a bomb with water at 250° C crystallized to a granular product having a mean index of refraction of 1.64. The X-ray pattern was similar in spacing and intensity of lines to that of a finely crystalline monohydrate of dicalcium silicate obtained by Keevil and Thorvaldson [19]. Treatment of a $2CaO:1SiO_2$ mixture of CaO and silica gel at 225° C (experiment 63) gave complete crystallization to the other monohydrated dicalcium silicate described by Thorvaldson and coworkers [18, 19]. This occurs in very small needles of low birefringence and mean index 1.60. Analysis gave a composition corresponding to the ratios $2.0CaO:1.0SiO_2:1.1H_2O$.

In experiments 64, 68, and 69 amorphous hydrated calcium silicate of CaO/SiO_2 molar ratio 3:2 was mixed with sufficient CaO to give a ratio of 2:1 and in the presence of water heated at temperatures of 225°, 300°, and 350° C. The principal product in all three cases was $CaO.SiO_2.H_2O$. The secondary product was not identified except in experiment 69, where the optical properties and X-ray pattern showed it to be a hydrate of tricalcium silicate.

(h) MOLAR RATIO CaO/SiO_2, 3:1

The results of these experiments are shown in table 9.

In experiment 71, 1 g of tricalcium silicate treated with 500 ml of water for 9 years at room temperature was completely converted to a hydrated material of composition $1.3CaO:1.0SiO_2:1.7H_2O$. Petrographic examination showed less than 5 percent of calcite with the bulk of the material appearing as rounded grains of low birefringence having refractive indices ranging from 1.52 to 1.53. The X-ray pattern of this material was different from that of calcite or any of the other hydrous or anhydrous calcium silicates thus far investigated.

TABLE 9.—*Results of experiments on* $3CaO:SiO_2$ *compositions*

Experiment number	Starting material	Temperature	Pressure	Time	Product
		°C	*atm*		
71	$3CaO.SiO_2$	25	1	9 years	?
72	do	100	1	14 days	$10CaO.5SiO_2.6H_2O+Ca(OH)_2$.
73	do	150	5	5 days	Do.
74	do	200	15	35 days	$3CaO.SiO_2.2H_2O+10CaO.5SiO_2.6H_2O+Ca(OH)_2$.
75	do	250	39	12 days	$3CaO.SiO_2.2H_2O$.
76	β-$2CaO.SiO_2+CaO$	250	39	10 days	$2CaO.SiO_2$ hydrate$+Ca(OH)_2$.
77	$3CaO:2SiO_2$:aq$+3CaO$	275	59	16 days	$3CaO.SiO_2.2H_2O$.
78	$3CaO.SiO_2$	350	163	8 days	Do.
79	do	450	397	6 days	Do.

Tricalcium silicate treated with water at 100° C under a reflux condenser (experiment 72) and in the bomb at 150° C (experiment 73)

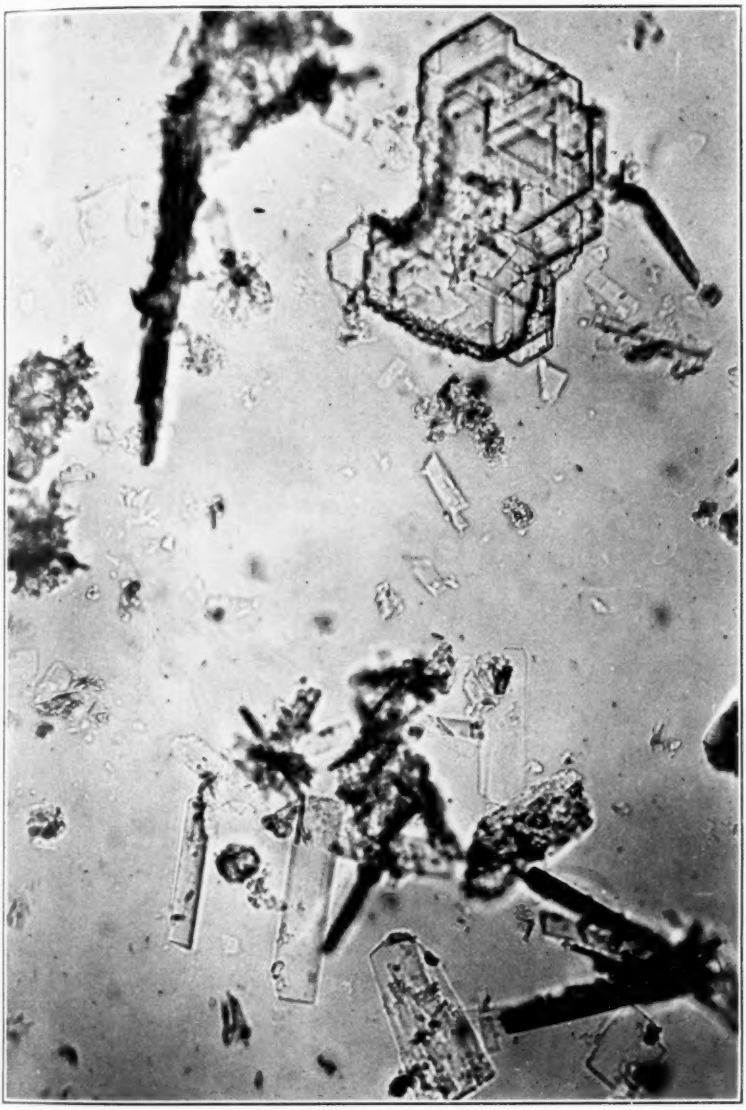

FIGURE 10.—*Lath-like orthorhombic plates of synthetic* $10CaO.5SiO_2.6H_2O$ *and hexagonal plates of* $Ca(OH)_2$ *obtained by treatment of portland cement clinker with water at 175° C.*

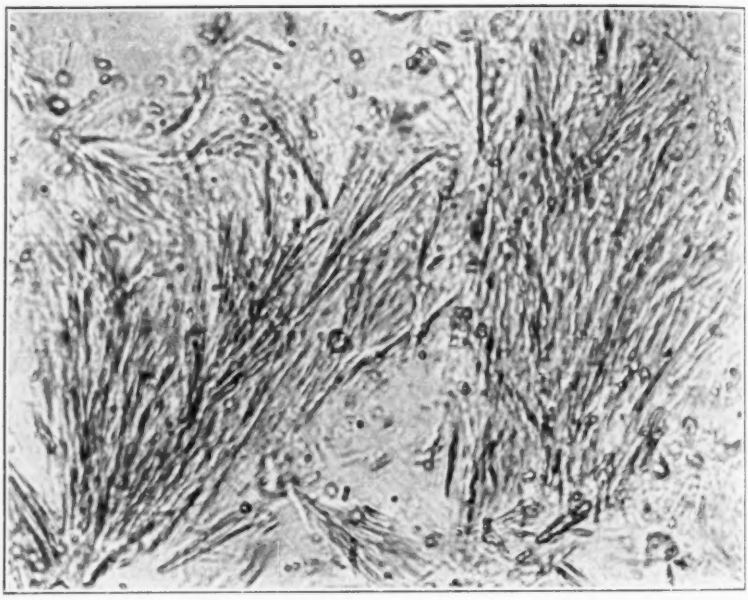

FIGURE 11.—*Synthetic* $3CaO.SiO_2.2H_2O$.
Magnification ×900.

was converted to $10CaO.5SiO_2.6H_2O$ and calcium hydroxide. At 250° C (experiment 75) direct hydration occurred without liberation of calcium hydroxide. The product consisted of broad fibrous crystals of positive elongation and parallel extinction. The indices of refraction were: $\alpha=1.590 \pm 0.003$, $\gamma=1.602 \pm 0.003$. Analysis of the preparation from experiment 75 gave the composition: 65.42 percent of CaO, 23.45 percent of SiO_2, 11.53 percent of H_2O, corresponding to the ratios: $2.98CaO:1.00SiO_2:1.63H_2O$. At 200° C (experiment 74) the product was primarily this compound with smaller amounts of $10CaO.5SiO_2.6H_2O$ and $Ca(OH)_2$ also present.

For experiment 77 the starting material was a mixture of amorphous hydrate of CaO/SiO_2 molar ratio 3:2 mixed with sufficient CaO to give a ratio of 3:1. After 16 days in the bomb at 275° C this preparation crystallized completely to large broom-shaped clusters of fibrous needles having the composition: 63.07 percent of CaO, 0.50 percent of R_2O_3, 22.38 percent of SiO_2, 13.56 percent of H_2O, corresponding to the ratios: $3.02CaO:1.00SiO_2:2.02H_2O$. A photomicrograph of this material is shown in figure 11. The X-ray pattern and optical properties were the same as those of the product from direct hydration of anhydrous tricalcium silicate. This preparation and that of experiment 75 gave negative tests for free lime by alcohol-glycerol extraction and by White's method.

This compound is identical with the product obtained by Keevil and Thorvaldson [19] by steaming tricalcium silicate between 110° and 375° C. By their procedure, however, only very finely crystalline material resulted.

Dehydration experiments proved the hydrated tricalcium silicate to be a very stable compound. A preparation heated in an oven for 16 hours at 215° C gave a loss in weight of only 0.2 percent. At 500° C for 16 hours the loss was 2.6 percent and at 700° C for 16 hours, 10.3 percent. Ignition for 5 minutes at 1,200° C gave complete conversion of the sample to β-dicalcium silicate and calcium oxide. Attempts to dehydrate the compound to tricalcium silicate were unsuccessful. Loss of water and liberation of free lime appear to take place concurrently.

In experiment 76 an attempt was made to prepare the hydrated tricalcium silicate from a $3CaO:1SiO_2$ mixture of β-$2CaO.SiO_2$ and CaO treated with water at 250° C. The product consisted of calcium hydroxide and the granular dicalcium silicate hydrate obtained by Keevil and Thorvaldson [19] and also identified in experiment 65, table 8 of this paper.

(i) MOLAR RATIO CaO/SiO_2, 4:1

Several experiments which were made to determine whether any hydrates richer in lime than $3CaO.SiO_2.2H_2O$ exist are recorded in table 10.

TABLE 10.—*Results of experiments on* $4CaO:1SiO_2$ *compositions*

Experiment number	Starting material	Temperature	Pressure	Time	Product
		°C	*atm*	*Days*	
79	β-$2CaO.SiO_2$+2CaO	250	39	7	$2CaO.SiO_2aq+Ca(OH)_2$
80	$3CaO.SiO_2+CaO$	250	39	12	$3CaO.SiO_2.2H_2O$.
81	$1.4CaO:SiO_2:aq+2.6CaO$	400	397	7	$3CaO.SiO_2.2H_2O+Ca(OH)_2$.
82	$1.3CaO:SiO_2:aq+2.7CaO$	450	400	6	$3CaO.SiO_2.2H_2O+Ca(OH)_2$.

The results indicate that dicalcium and tricalcium silicates form the same hydrates as they did in the absence of excess lime. The dicalcium silicate hydrate formed in experiment 79 occurred in small irregular plates having refractive indices ranging from 1.62 to 1.64. It was the same product as was obtained in experiment 76, table 9, and experiment 65, table 8 of this paper.

5. CEMENTITIOUS MATERIAL IN SAND-LIME BRICK

Some experiments similar to those of Grime and Bessey [2] were made in an attempt to isolate the hydrated calcium silicate in a commercial sand-lime brick of good quality. Half of the brick was crushed in a porcelain mortar with as little grinding as possible. Of this material the sample passing a No. 40 sieve and retained on a No. 70 sieve after brief shaking was used. It contained 4.4 percent of soluble silica determined according to the usual procedure. The material was screened on a No. 200 sieve for ½ hour and that passing was examined under the microscope. It appeared to consist almost wholly of calcite and was discarded. Screening was then continued another half hour. It was hoped by this method that the cementing material surrounding the sand grains might be rubbed off and concentrated. That this apparently occurred was shown by an increase in soluble silica to 16.2 percent in the material passing the No. 200 sieve. A number of pennies were then added to the material on the No. 200 sieve to assist the rubbing action, and the screening was continued for an hour. The material passing then showed a soluble silica content of 20.2 percent. However, in the X-ray patterns of both samples only the lines of calcite and quartz appeared.

It was thought that evidence of the presence of a crystalline hydrated calcium silicate might be obtained using a laboratory-prepared brick. For this purpose a mixture of 10 percent of hydrated lime and 90 percent of graded Ottawa sand (containing 0.13 percent of soluble silica) was molded into a bar in a hand press. The bar was then treated in contact with water at 175° C for 20 hours. After crushing the brick, the whole sample was found to contain 2.6 percent of soluble silica. This sample was rubbed with the fingers on a No. 20 sieve and the material passing in each case was rubbed successively on the No. 48, 100, and 200 sieves. The material passing the No. 200 sieve contained 16.8 percent of soluble silica. In the X-ray pattern the strongest lines were those of calcium hydroxide together with the lines of quartz.

Another bar was treated in the bomb at 175° C for 15 days. After a separation similar to that just described the material passing a No. 200 sieve was extracted for 75 hours with boiling ethylene glycol in an extractor of the type used in rubber analysis. The residue contained no free calcium hydroxide. Its X-ray pattern showed the lines of quartz with a few additional lines of moderate intensity which did not coincide with any of the lines of quartz, calcite, or calcium hydroxide. It was not possible, however, to assign these additional lines with certainty to any of the known hydrated calcium silicates.

IV. DISCUSSION

In the manufacture of sand-lime brick a wetted mixture of about 10 percent of hydrated lime and 90 percent of sand is pressed into forms, the resulting blocks removed, and steamed in an autoclave at 150° to 200° C (5 to 15 atm) for 8 to 12 hours. The nature of the cementing material formed by this treatment has never been established, but it is presumed to be a hydrated calcium silicate. X-ray and optical data [2] indicate that it may be amorphous. Some inferences regarding its potential crystalline composition may, however, be made from the results of this paper.

Lime usually constitutes only about 10 percent of the sand-lime brick mix, but its proportion to surface silica available for reaction will evidently be much higher owing to the relative coarseness of the sand particles. Thus, it is probable that the cementing material of the brick will be much richer in lime than the mix as a whole. Such a condition might permit the crystallization of compounds as highly basic as $10CaO.5SiO_2.6H_2O$. This compound appears to be by far the most easily formed of the hydrated calcium silicates at the temperatures employed in sand-lime brick manufacture. However, if the lime available for reaction with surface silica is insufficient to form this compound the potential crystallization of a less basic compound such as gyrolite might be favored.

Although the experiments with sand-lime brick failed to establish the identity of the cementing material in sand-lime brick, the greatly increased soluble silica content of the finer fractions of the crushed brick appears to indicate the formation of potentially crystalline compounds. That these combinations could not be identified by their X-ray patterns is not surprising in view of the fact that the various syntheses described in this paper all required much longer periods of time than those employed in sand-lime brick manufacture. The appearance of additional lines in the X-ray pattern of the sand-lime brick treated for a longer period is promising, and it is hoped that further work may reveal their source.

The crystalline materials obtained by reaction of water on β-dicalcium silicate and tricalcium silicate at room temperature are noteworthy with reference to end products in the setting of portland cement. There is a possibility that the product derived from dicalcium silicate, and which had a composition approximating $3CaO.2SiO_2.1.5H_2O$ on complete crystallization, may occur in set portland cement. This product could not be identified with any of the known calcium hydrosilicate minerals.

The poorly crystallized material which resulted from treatment of tricalcium silicate with water at room temperature had a CaO/SiO_2 molar ratio of only 1.3 owing to the extensive hydrolysis which had taken place in the presence of a large excess of water. Therefore, it probably would not form in the setting of portland cement when less water is used but might occur in hydrated puzzolanic cement where the proportion of silica to lime is higher. Unfortunately, the pattern of this material also could not be identified.

As has been pointed out by Thorvaldson and coworkers [17, 18, 19], the compounds designated in this paper as $10CaO.5SiO_2.6H_2O$ and $3CaO.SiO_2.2H_2O$ are probable products of the autoclave treatment of portland cements. Under such conditions it has also been

shown by Mather and Thorvaldson [20] that tricalcium aluminate will hydrate to $3CaO.Al_2O_3.6H_2O$ and tetracalcium aluminoferrite to $3CaO.Al_2O_3.6H_2O$ and $CaO.Fe_2O_3$ hydrate, which, in turn, will slowly decompose to $Ca(OH)_2$ and hematite. Thus it would appear possible to hydrate cement partially in the autoclave without the liberation of appreciable free lime. This is actually the case. A group of four high-tricalcium silicate cements all having ignition losses and free-lime contents of less than 1 percent was steamed in the autoclave at 200° C (15 atm) overnight. The ignition loss in each case was increased to 5 to 6 percent. The free-lime content of one cement remained the same, another showed a slight decrease, and the two remaining, an increase of a few tenths of a percent.

With regard to the 215° C autoclave test [1] for neat cement bars, the fact that calcium hydroxide can react with amorphous hydrated calcium silicate already formed, to give the hydrate of tricalcium silicate, is significant. This result, taken in conjunction with those of Mather and Thorvaldson [20], indicates that any expansion which results from autoclaving cannot be caused by crystallization of calcium hydroxide liberated from the cement compounds, but must be ascribed to other causes.

As was pointed out with reference to sand-lime brick, the crystallization of hydrated calcium silicates occurs slowly, requiring days or weeks to reach completion even at temperatures above 200° C. It is not to be expected, therefore, that well-developed crystals of any of the various hydrates described in this paper would be found in specimens steamed for the short period employed in the autoclave test. Only incipient crystallization would occur, but the products should be the same as those formed over longer periods.

V. SUMMARY

Table 11 gives a summary of optical properties of the natural and synthetic minerals identified in this investigation.

X-ray study of the hydrated calcium silicate minerals indicated that the following are distinct compounds:

Okenite	$CaO.2SiO_2.2H_2O$.
Gyrolite	$2CaO.3SiO_2.2H_2O$.
Crestmoreite	$2CaO.2SiO_2.3H_2O$.
Xonotlite	$5CaO.5SiO_2.H_2O$.
Afwillite	$3CaO.2SiO_2.3H_2O$.
Foshagite	$5CaO.3SiO_2.3H_2O$.
Hillebrandite	$2CaO.SiO_2.H_2O$.

Centrallasite, $4CaO.7SiO_2.5H_2O$, and truscottite, $4(Ca,Mg)O.7SiO_2.5H_2O$, seem to be impure forms of gyrolite. Riversideite, $2CaO.2SiO_2.H_2O$, is apparently not a distinct mineral and is probably the same compound as crestmoreite.

Preparations having X-ray patterns identical with those of gyrolite, xonotlite, and foshagite were synthesized by hydrothermal methods. Other compounds formed were cristobalite, wollastonite, pseudowollastonite, β–$3CaO.2SiO_2$, $4CaO.5SiO_2.5H_2O$, $CaO.SiO_2.H_2O$, $2CaO.SiO_2.H_2O$, $10CaO.5SiO_2.6H_2O$, and $3CaO.SiO_2.2H_2O$.

TABLE 11.—*Optical properties of natural and synthetic minerals identified in this study*

Composition	Optical properties					Crystal system and habit	Elongation	Mineral name	Obtained synthetically
	Sign	Optic angle	α or ω	β	γ or ϵ				
$CaO.2SiO_2.2H_2O$	−	Large	1.530		1.541	Orth. fibrous.	+	Okenite	No.
$2CaO.3SiO_2.2H_2O$	−	0	1.548		1.536	Trig. fibrous lamellae.	+	Gyrolite	Yes.
$4CaO.5SiO_2.5H_2O$				1.54		Acicular	+	Tobermorite(?)	Yes.
$5CaO.5SiO_2.H_2O$	+	Small	1.583	1.583	1.594	Orth. (?) fibrous.	+	Xonotlite	Yes.
$CaO.SiO_2.H_2O$				1.603		(?)	−		Yes.
$2CaO.2SiO_2.3H_2O$	−	Large	1.593	1.603	1.607	Fibrous	+	Crestmoreite	No.
$3CaO.2SiO_2.1.5H_2O$				1.60		do			Yes.
$3CaO.2SiO_2.3H_2O$	+	54°	1.617	1.620	1.634	Mon. prism.	−	Afwillite	No.
$5CaO.3SiO_2.3H_2O$	+	Small	1.594	1.594	1.598	Orth. fibrous.	+	Foshagite	Yes.
$2CaO.SiO_2.H_2O$	−	60° to 80°	1.605	1.61	1.612	do	+	Hillebrandite	No.
$2CaO.SiO_2.H_2O$				1.60		(?)	+		Yes.
$2CaO.SiO_2.H_2O$				1.64		(?)			Yes.
$10CaO.5SiO_2.6H_2O$	+	Medium	1.614	1.620	1.633	Orth	+		No.
$6CaO.3SiO_2.2H_2O$			1.642		1.672	(?)			Yes.
$3CaO.SiO_2.2H_2O$			1.590		1.602	Fibrous	+		Yes.

Attempts to produce okenite synthetically were unsuccessful. Thus, a sample of calcium disilicate glass treated with water for 8 weeks at 150° C gave partial crystallization to cristobalite only.

Gyrolite was formed at 150° to 400° C from glasses and amorphous hydrates having CaO/SiO_2 molar ratios in the vicinity of 2:3.

Treating amorphous hydrate with CaO/SiO_2 molar ratio 0.80 at temperatures between 150° and 275° C gave a single phase of distinctive X-ray pattern, and a composition corresponding to $4CaO.5SiO_2.5H_2O$. This composition is similar to that reported for the rare mineral tobermorite. At 300° C the product was xonotlite.

Amorphous monocalcium silicate hydrate at 150° C crystallized to $CaO.SiO_2.H_2O$, which had a distinctive X-ray pattern. However, in the presence of higher molar ratios of lime to silica, $CaO.SiO_2.H_2O$ was formed at temperatures as high as 350° C.

Xonotlite, $5CaO.5SiO_2.H_2O$, crystallized from preparations of amorphous hydrated monocalcium silicate between 165° ±15° C and 395° ±5° C (70 to 225 atm). Above 395° C wollastonite crystallized.

Amorphous hydrate of molar ratio $3CaO/2SiO_2$ treated between 150° and 400° C did not yield afwillite, $3CaO.2SiO_2.3H_2O$, but instead crystallized partially to $CaO.SiO_2.H_2O$ at the lower temperatures and to xonotlite at the higher. These were probably metastable crystallizations resulting from the relatively high crystallization potential of the monocalcium silicate hydrates. Anhydrous tricalcium disilicate treated at 250° C was converted to an unidentified hydrate.

The usual form of anhydrous tricalcium disilicate treated at 500° C (380 atm) for 2 weeks was converted to a low-temperature or β form of the anhydrous compound. It inverts to the high-temperature form at 1,024° ±5° C.

Glass of composition $5CaO.3SiO_2$ treated at 300° and 350° C was converted to a product having an X-ray pattern identical with that of the mineral foshagite.

The compound $10CaO.5SiO_2.6H_2O$ was formed from β- and γ-dicalcium silicates, tricalcium silicate, and mixtures of lime and silica gel in the temperature range 100° to 200° C. Attempts to prepare a hydrate identical with natural hillebrandite were unsuccessful.

Tricalcium silicate treated with water between 200° and 450° C hydrated directly to $3CaO.SiO_2.2H_2O$. No hydrates of higher lime content than $3CaO.SiO_2.2H_2O$ appear to exist.

A number of unsuccessful attempts were made to isolate and identify the cementing material in sand-lime brick.

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CALCULATION OF STRESSES AND NATURAL FREQUENCIES FOR A ROTATING PROPELLER BLADE VIBRATING FLEXURALLY

By Walter Ramberg and Sam Levy

ABSTRACT

The present paper extends the method of computing the natural modes of flexural vibration of a nonrotating propeller blade which was described in RP764 to blades that rotate as in actual flight. The resulting integral equations were solved for two aluminum-alloy propeller blades of typical design vibrating with the fundamental mode and with the second harmonic mode and rotating at speeds covering the range of service speeds. The effect of rotation on the stress distributions and on the natural frequencies was obtained for the two extreme end conditions of rigid clamping at the hub and no clamping at the hub. Rotation was found to have a small effect (up to 13 percent) on the maximum stress per unit tip deflection and was found to shift the maximum toward the hub. For the determination of critical speeds, the natural frequencies were shown to follow conveniently from Lord Rayleigh's energy method by making use of the solutions for no rotation outlined in RP764. The effect of initial twist on the flexural frequencies of the blade was found to be small compared with the effect of changes in clamping at the hub. Changes in clamping may change the frequency up to 13 percent. A correction to RP764 is noted in this connection. Both the stress distribution and the natural frequencies of a given propeller blade may be calculated from those obtained for a model blade by means of two model rules developed by Theodorsen.

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I. PURPOSE OF INVESTIGATION

The determination of stresses in a nonrotating propeller blade vibrating with a flexural mode has been discussed in Bureau Research Paper RP764 [1].[1] In that paper it was shown that the bending stresses set up in the blade could be conveniently determined from strain measurements on the surface of the blade, after the blade had been set into resonance with the desired flexural mode. The stresses so determined were found to agree closely with those calculated from the theory of flexural vibrations for beams of variable section. Fatigue failures in the center portion of eight aluminum-alloy blades were produced by vibrating the blades at the fundamental mode with a sufficiently high amplitude to produce a crack after 33,800 to 2,390,000 cycles of vibration. The crack occurred in every case at a maximum stress amplitude greater than 14,000 pounds per square inch, and at a point where the stress differed only a few percent from the measured maximum stress. Attempts to produce fatigue failures near the tip in blades vibrating with the second harmonic mode were not successful, mainly because a sufficiently high stress amplitude could not be maintained in the blade. Within the last few months one such fatigue failure was obtained in an aluminum-alloy blade while it was being used to calibrate certain dynamic-strain gages. The fatigue crack extended through about 85 percent of the cross-sectional area of the blade and developed at a distance of 13 inches from the tip at a point within an inch of the location at which the maximum stress amplitude had been measured.

The results of tests on nonrotating blades can be applied to propellers in flight only if the effect of centrifugal force on the natural modes of vibration is clearly understood. A number of investigations have already been made to determined the effect of an angular speed, ω, on the natural frequency, p, of the blade, and a formula of the type

$$p^2=p_0^2+\alpha\omega^2(\text{rad}^2/\text{sec}^2) \tag{1}$$

was proposed as early as 1918 by Berry [2]. Values of the constant α ranging from 1.04 to 1.9 have been obtained by various investigators [3, 4, 5, 6, 7, 8, 9]. The large variation in the values of α may be ascribed, principally, to differences in the design of the propeller blade. The constant α was determined theoretically as 1.19 for the uniform beam vibrating with its fundamental mode, by Berry [2], and as 1.4 for a wedge, by Webb and Swain [3]. Hansen and Mesmer [7] concluded, on the basis of tests, that α is about 1.45 for blades of usual design. Theodorsen obtained a considerably higher value (α=1.9), also on the basis of tests (revision of values given in [9].)

The effect of centrifugal force on the stress distribution in a rotating blade vibrating with a flexural mode has not been studied as extensively as the effect on the natural frequencies. An experimental determination of the stress distribution has not been possible until very recently, since no dynamic strain gages were available which could be attached to a rotating blade and which could be expected to give a fairly accurate value of the strain amplitude during lateral vibrations. In addition, the problem of exciting a single

[1] Figures in brackets indicate the literature references at the end of this paper.

flexural mode in a rotating blade is not a simple one; up to the present time it has been solved only for a thin model blade rotating at a relatively low speed [9].

Until the experimental difficulties just mentioned have been overcome, an answer to the problem can only be expected from a theoretical attack. The close agreement between measured and calculated stress distributions and natural frequencies for nonrotating blades suggested that an extension of the solution to rotating blades would give equally reliable results on the effect of rotation on both stress distribution and natural frequencies.

The present paper deals with the extension of the theoretical method originally developed by Hansen and Mesmer [7, 1] to rotating blades and gives the resulting stress distributions and natural frequencies for two aluminum-alloy propeller blades of different design.

II. CALCULATION OF STRESSES

1. EQUATION OF MOTION OF IDEALIZED STRAIGHT PROPELLER BLADE

It will be assumed, as in the case of the nonrotating blade [1], that the flexural vibrations of the propeller blade may be adequately represented by the motion of a straight beam whose cross-sectional areas and principal moments of inertia are equal to those of the propeller blade, and whose principal axes of inertia remain parallel throughout the length of the beam. The ordinary beam theory may then be applied in setting up the equation of motion of the blade for the case of resonant vibration in the fundamental mode and the second harmonic mode.

The adequacy of this approximation as applied to nonrotating propeller blades was confirmed by the close agreement that was found [1] between the stress distribution and the frequency of the actual blade with its initial twist and initial curvature and the corresponding stress distributions and frequencies for the idealized straight blade. Its adequacy for determining the fundamental frequency and second harmonic frequency of rotating blades is confirmed by the close agreement between the experimental frequencies determined by Theodorsen (revision of values given in [9]) and the frequencies calculated assuming an idealized straight propeller blade (see fig. 17, page 660).

No data are available to verify the assumption that the stress distribution for the fundamental mode and the second harmonic mode of the rotating blade is not affected by the initial twist. Strain measurements to check this assumption are desirable.

A small section of the idealized straight blade of length Δx (fig. 1) will be in equilibrium in the z-direction under the action of two forces; (1) the inertia force $\rho A\ddot{z}\Delta x$, where ρ is the density and A is the cross-sectional area of the blade; and (2) the restoring force in the z-direction tending to bring the blade back to its mean position due to the tension, T, and shear, Q. This condition may be expressed mathematically by

$$\frac{\partial}{\partial x}(T \sin \theta + Q \cos \theta)\Delta x = \rho A\ddot{z}\Delta x. \tag{2}$$

For small deflections, only terms of the first order in θ need be retained, so that $\sin\theta=\partial z/\partial x$, $\cos\theta=1$ and therefore eq 2 may be written as

$$\frac{\partial}{\partial x}\left(T\frac{\partial z}{\partial x}+Q\right)\Delta x=\rho A\ddot{z}\Delta x. \tag{3}$$

The ordinary beam theory gives with the same degree of approximation

$$Q=-\frac{\partial}{\partial x}EI\frac{\partial^2 z}{\partial x^2}. \tag{4}$$

The tension, T, at x due to centrifugal force is for small deflections ($\cos\theta=1$) given by the sum of the tensions $\rho Ax\Delta x\omega^2$ due to the particles lying between section x and the tip of the blade. This leads to the integral

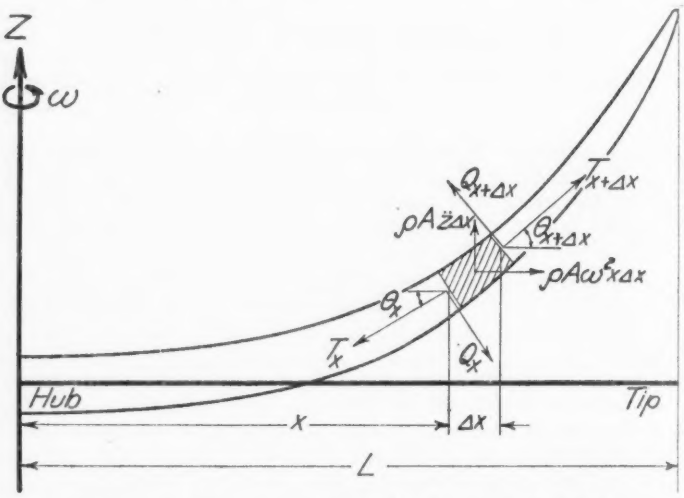

FIGURE 1.—*Forces on portion of rotating propeller blade.*

$$T=\rho\omega^2\int_x^L Axdx. \tag{5}$$

Substituting eq 4 and 5 in eq 3, and dividing through by Δx, gives the following differential equation for the motion of a rotating beam vibrating flexurally

$$\frac{\partial}{\partial x}\left[-\frac{\partial}{\partial x}\left(EI\frac{\partial^2 z}{\partial x^2}\right)+\rho\omega^2\frac{\partial z}{\partial x}\int_x^L Axdx\right]-\rho A\ddot{z}=0. \tag{6}$$

During a natural vibration of a blade, each of its sections will vibrate sinusoidally with the natural frequency, p, of the mode considered. If X is the amplitude of motion of the section, its motion may be described by

$$z=X\sin pt. \tag{7}$$

The substitution of eq 7 in eq 6 leads to the following differential equation for the natural modes of flexural vibration of a rotating blade:

$$\frac{d}{dx}\left[-\frac{d}{dx}\left(EI\frac{d^2X}{dx^2}\right)+\rho\omega^2\frac{dX}{dx}\int_x^L Axdx\right]+\rho Ap^2X=0. \tag{8}$$

It is convenient in considering solutions of this equation to introduce the following dimensionless variables and the constant k:

$$\xi=\frac{x}{L},\quad \eta=\frac{X}{L},\quad f=\frac{A}{L^2},\quad i=\frac{I}{L^4},\quad k=\frac{\rho L^2p^2}{E},\quad u=\int_\xi^1 f\xi d\xi. \tag{9}$$

The ratios are proportional as follows: ξ, to the distance from the axis of rotation of the section considered; η, to the amplitude at the section; f, to the cross-sectional area; i, to the moment of inertia; k, to the square of the natural frequency; and u, to the centrifugal tension. In terms of these variables, eq 8, after a simple transformation, becomes

$$\frac{d^2}{d\xi^2}i\eta''=k\left(f\eta+\frac{\omega^2}{p^2}\frac{d}{d\xi}(u\eta')\right), \tag{10}$$

where the prime denotes differentiation with respect to ξ.

The amplitude of the bending moment at any section,

$$M=EI\frac{d^2x}{dx^2}=EL^3i\eta'', \tag{11}$$

may be derived from this equation by integrating twice with respect to ξ. The two constants of integration are fixed by the boundary conditions of zero shear and zero bending moment at the tip. These are,

$$\xi=1,\ \frac{d}{d\xi}(i\eta'')=0,\ i\eta''=0. \tag{12}$$

Integrating eq 10, and substituting the boundary conditions, in eq 12, gives

$$i\eta''=k\left[\int_\xi^1\int_\xi^1 f\eta d\xi d\xi-\frac{\omega^2}{p^2}\int_\xi^1 u\eta' d\xi\right]. \tag{13}$$

The first integral on the right denotes the bending moment due to inertia forces, while the second integral is the restoring moment due to the centrifugal forces. This latter restoring moment is found to increase with the square of the speed of rotation of the blade. It adds materially to the stiffness of the blade at speeds of rotation approaching operating speeds.

The extreme fiber bending stress, σ_x, is according to the ordinary beam theory,

$$\sigma_x=\frac{Mc}{I}=\frac{c}{L}E\eta'', \tag{14}$$

where c is the distance of the fiber from the neutral axis of the section, and η'' is as given by eq 13.

An integral equation for the amplitude curve $\eta(\xi)$ can be obtained by integrating eq 13 twice again and using the proper boundary conditions at the hub. These boundary conditions will depend upon the type of exciting forces and restraints. Because of the twist in propeller blades, the natural modes are neither purely symmetric nor purely antisymmetric. However, the motion for the lower-frequency modes is mainly parallel to the shaft, and the types of motion may be classified according to the symmetry or antisymmetry of this component.

Modes excited by forces at the center of the hub in the plane of rotation and modes excited by moments about axes in this plane will have components normal to this plane which are antisymmetric, while modes excited by forces at the hub parallel to the shaft and modes excited by moments about the shaft will have components normal to the plane of rotation, which are symmetric. Since the principal source of vibration in propellers is believed to be torque variation in the shaft, only the second type of motion is considered important. On this account, only symmetric modes in the idealized straight propeller are considered in this paper.

Integrating eq 13 twice for a symmetrical mode of vibration, that is, a mode of vibration satisfying the end condition,

$$\xi=0,\ \eta'=0, \tag{15}$$

gives the equation

$$\eta=\eta_0+k\int_0^\xi\int_0^\xi\frac{1}{i}\left[\int_\xi^1\int_\xi^1 f\eta d\xi d\xi-\frac{\omega^2}{p^2}\int_\xi^1 u\eta' d\xi\right]d\xi d\xi. \tag{16}$$

The constant of integration η_0, which corresponds to the deflection at the hub, will depend on the restraint at the hub. The hub restraint at the root of each blade may be approximated by setting it equal to that due to a concentrated mass, M, rigidly attached to the hub combined with an elastic restraint against axial motion with a spring constant, S. The harmonic motion with an amplitude $X_0=L\eta_0$ of the mass, M, will apply a deflecting force with an amplitude MX_0p^2 to the hub, while the elastic restraint applies a restoring force with an amplitude SX_0. Balancing the resultant of these forces by the shear in the hub section of the blade gives

$$MX_0p^2-SX_0=\left[\frac{d}{dx}\left(EI\frac{d^2X}{dx^2}\right)\right]_{x=0}. \tag{17}$$

It is convenient to express M and S in terms of the ratios,

$$m=\frac{M}{\rho L^3},\ s=\frac{S}{\rho L^3p^2}, \tag{18}$$

so that eq 17 becomes with eq 9,

$$\eta_0(m-s)=\left[\frac{1}{k}\frac{di\eta''}{d\xi}\right]_{\xi=0}. \tag{19}$$

It will be noticed from eq 13 that for a symmetrical mode, $\eta'(0)=0$,

$$\frac{1}{k}\left[\frac{di\eta''}{d\xi}\right]_{\xi=0}=-\int_0^1 f\eta d\xi, \tag{20}$$

so that eq 19 becomes

$$\eta_0(m-s)=-\int_0^1 f\eta d\xi. \tag{21}$$

This equation evidently expresses the equilibrium between the concentrated transverse force applied at the hub and the distributed transverse inertia forces due to the vibration of the blade integrated from the hub to the tip. Substitution from eq 16 for the right-hand side of eq 21 leads to an equation which may be solved for η_0. Substituting the resulting value of η_0 in eq 16 leads to the following integral equation for symmetrical flexural modes of vibration:

$$\eta=k\left\{\int_0^\xi\int_0^\xi\frac{1}{i}\left[\int_\xi^1\int_\xi^1 f\eta d\xi d\xi-\frac{\omega^2}{p^2}\int_\xi^1 u\eta' d\xi\right]d\xi d\xi\right. \tag{22}$$
$$\left.-\frac{1}{m-s+\int_0^1 f d\xi}\int_0^1 f\left(\int_0^\xi\int_0^\xi\frac{1}{i}\left[\int_\xi^1\int_\xi^1 f\eta d\xi d\xi-\frac{\omega^2}{p^2}\int_\xi^1 u\eta' d\xi\right]d\xi d\xi\right)d\xi\right\}.$$

Numerical solutions of this integral equation were obtained for two special cases only; (1), the case of rigid clamping (fixed-free blade), which corresponds to infinite values of $m-s$, so that eq 22 becomes

$$\eta=k\left\{\int_0^\xi\int_0^\xi\frac{1}{i}\left[\int_\xi^1\int_\xi^1 f\eta d\xi d\xi-\frac{\omega^2}{p^2}\int_\xi^1 u\eta' d\xi\right]d\xi d\xi\right\}; \tag{23}$$

and (2), the case of no clamping (free-free blade), which corresponds to $m-s=0$, so that eq 22 becomes

$$\eta=k\left\{\int_0^\xi\int_0^\xi\frac{1}{i}\left[\int_\xi^1\int_\xi^1 f\eta d\xi d\xi-\frac{\omega^2}{p^2}\int_\xi^1 u\eta' d\xi\right]d\xi d\xi\right. \tag{24}$$
$$\left.-\frac{1}{\int_0^1 f d\xi}\int_0^1 f\left(\int_0^\xi\int_0^\xi\frac{1}{i}\left[\int_\xi^1\int_\xi^1 f\eta d\xi d\xi-\frac{\omega^2}{p^2}\int_\xi^1 u\eta' d\xi\right]d\xi d\xi\right)d\xi\right\}.$$

It is interesting to note that the boundary condition $m-s=0$ for a free-free blade may be satisfied theoretically in the presence of elastic restraint at the hub, provided the concentrated mass at the hub is such as to balance the spring force at the natural frequency in question.

The solutions, eq 23 and 24, will bound all those natural modes for which $m-s\geq 0$, that is, they apply to the symmetrical flexural modes in a two-blade propeller whose hub acts like a concentrated mass, $M_0=\rho L^3(m-s)$. In the remaining cases in which the propeller hub acts like a spring with an equivalent spring constant, $S_0=\rho L^3 p^2(s-m)$, the frequency will, in general, lie outside of the values determined by eq 23 and 24. If, for example, in eq 22 $m-s$ is given a large but finite negative value, the solution will have a frequency below that determined by eq 23; while if $m-s$ is given a small negative value, the frequency will be above that determined by eq 24.

Experiments indicate that the natural flexural modes of nonrotating propellers [1] are bounded by the particular solutions in eq 23 and 24 with $\omega=0$. Propeller hubs of practical design seem to act

like a concentrated mass rather than like a concentrated spring. It was decided, accordingly, to confine the theoretical work on the rotating blade to solutions of eq 23 and 24 for certain propeller blades of practical design. The resulting modes were found to be sufficiently similar for the two boundary conditions of rigid clamping and no clamping at the hub, as expressed by eq 23 and 24, to make it probable that they are adequate expressions for the flexural modes of the blades in a multiple-blade propeller as well as in a two-blade propeller.

2. MODE OF MOTION AND STRESS DISTRIBUTION FOR FUNDAMENTAL MODE

Equations 23 and 24 may be solved for the fundamental mode, and the stress distribution for this mode, by using a procedure that is a direct extension of the corresponding procedure for nonrotating propeller blades, as described in detail in Bureau Research Paper RP764 [1]. The deflection curve η for the fundamental mode for a given value of the ratio ω/p is obtained by assuming a deflection curve η which approximates roughly the shape of the expected deflection curve, substituting the assumed value of η on the right-side of eq 23 or 24 and carrying out the integration by the numerical procedure described in detail in [1]. This will, in general, lead to a value of η/k which approximates the shape of η for the fundamental mode more closely than the initially assumed shape of η. The integration is repeated after inserting on the right-hand side of the equation a deflection curve proportional to the deflection curve η/k just calculated, until the integral η/k has the same shape as the η in the integrand on the right. The constant of proportionality, k, will then give the angular frequency, p, of the blade, and knowing p, one may calculate the speed of rotation, ω, from the initially assumed value of ω/p. The calculation was found to converge to the correct solution after two or three cycles of integration when the initial η was taken as the deflection curve of the propeller blade without rotation. With the calculation of the deflection curve for the fundamental mode of vibration the stress distribution may be determined by substituting the integral, eq 13, which is evaluated automatically as one of the steps in the integration of eq 23 or 24, in the stress formula, eq 14.

It should be noted from eq 23 and 24 that ω/p must be below a certain value in order to lead to a positive value of k and hence a real natural frequency, p. This limiting value of ω/p corresponds to the asymptote to the curve of $p=f(\omega)$ for infinitely high speeds of rotation, ω. In propeller blades of usual design the asymptotic portion of the curve lies far beyond the range of operating speeds; the limiting value of ω/p is, therefore, not of practical importance in this connection.

The above procedure was used to determine fundamental modes of vibration and stress distributions corresponding to these modes for aluminum-alloy blades of two typical designs. One design, which is referred to as type 32, had already been used to study flexural vibrations of a nonrotating blade [1]. The other design will be referred to as type 4371. A model blade of this design was used by Theodorsen [9] to determine the natural frequencies of flexural vibration with rotation. The radius, L (distance from center of hub to tip), for a propeller blade of type 32 was equal to 47.6 inches, while it was equal to

66 inches for a blade of type 4371. The cross-sectional area, A, the moment of inertia, I, the centrifugal-force ratio, u, and the extreme fiber distance, c, for the convex side for any section were evaluated

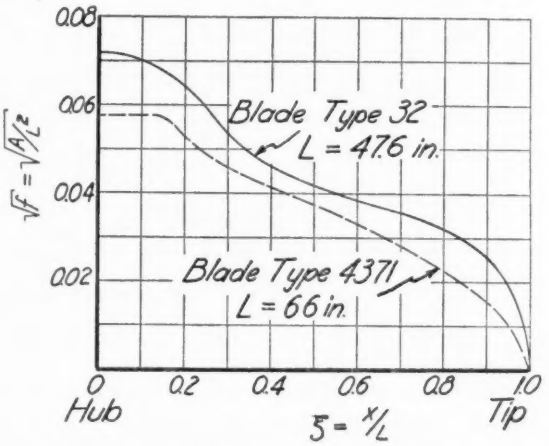

FIGURE 2.—*Distribution of* $(A/L^2)^{1/2}$ *along propeller blades of type 32 and type 4371, where* A *= cross-sectional area at distance* x *from center of hub and* L *= length of blade.*

from the design data for the two types of blades and were used to plot the curves of $f^{1/2}$, $i^{1/4}$, $u^{1/2}$, and c/L shown in figures 2 to 5. Figure 6 shows the ratio u/f, which is proportional to the stress due to centrifugal force.

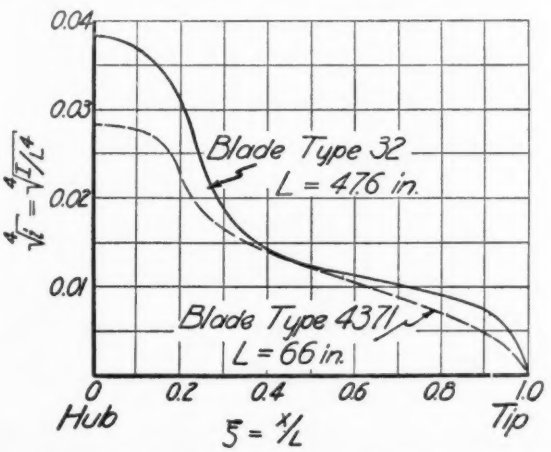

FIGURE 3.—*Distribution of* $(I/L^4)^{1/4}$ *along propeller blades of type 32 and type 4371, where* I *= minimum moment of inertia at distance* x *from center of hub and* L *= length of blade.*

Figure 7 gives the shape of the fundamental mode for a blade of type 32 calculated from eq 23 for speeds between 0 and 2,250 rpm, assuming clamping at the center of the hub. The effect of centrifugal

force is clearly seen in reducing the curvature in the tip portion of the blade and in shifting the point of maximum curvature toward the hub.

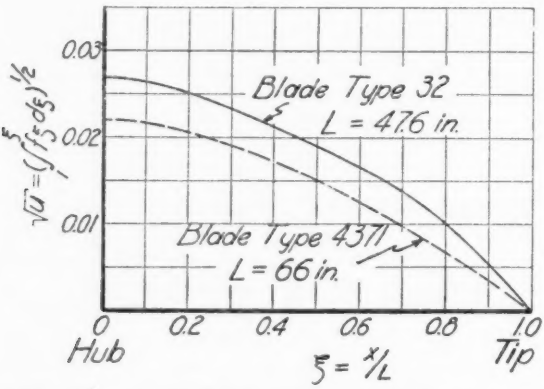

FIGURE 4.—*Distribution of $u^{1/3}$ along propeller blades of type 32 and type 4371, where $u=(1/L^4)\int_x^L Axdx$=centrifugal-force ratio at section at a distance x from center of hub, A=cross-sectional area, and L=length of blade.*

Figure 8 shows the corresponding result for a blade of type 4371 for speeds of rotation of 0, 860, and 2,020 rpm.

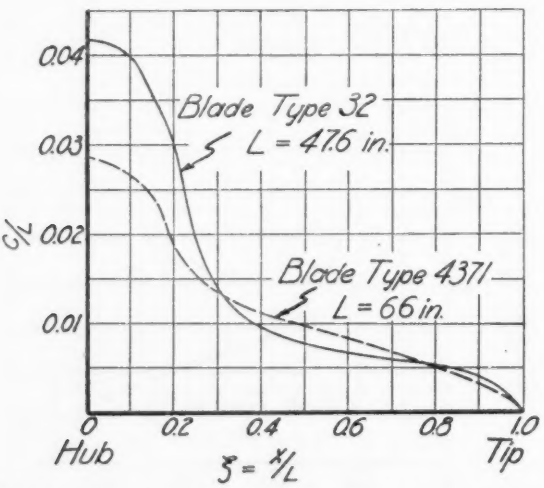

FIGURE 5.—*Distribution of c/L along propeller blades of type 32 and type 4371, where c=extreme fiber distance for convex side along center line of blade at a distance x from center of hub and L=length of blade.*

Figure 9 shows the shape of the fundamental mode for a blade of type 32, as calculated from eq 24, for the condition of zero fixity at the hub for speeds of rotation of 0 and of 1,620 rpm. Rotation has a very small effect on the shape of the mode in this case.

The effect of rotation on the shape of the stress-distribution curve for the fundamental mode is brought out in figures 10 to 12.

Figure 10 gives the stress distribution along the center line on the convex side for a blade of type 32 clamped at the center of the hub for

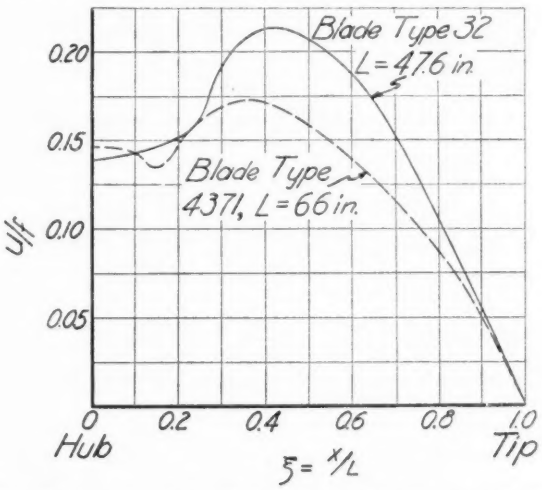

FIGURE 6.—*Distribution of centrifugal stress ratio u/f along propeller blades of type 32 and type 4371; for definition of u and f, see figures 4 and 2; L=length of blade.*

speeds of rotation between 0 and 2,250 rpm. The point of maximum stress amplitude is shifted towards the hub by the stiffening action of the centrifugal force. At the same time, the maximum stress per inch

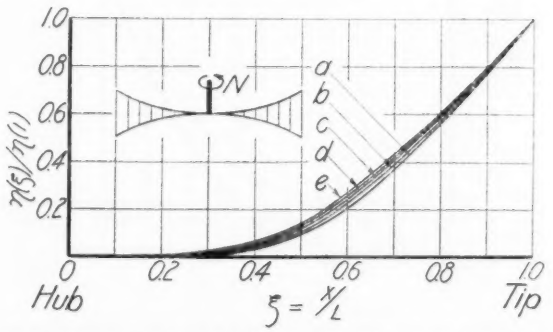

FIGURE 7.—*Deflection curves for fundamental mode of blade type 32 clamped at center of hub, rotating at a speed N, and vibrating with a frequency f.*

Curve *a*, N=0 rpm, f=30.6 c/s; curve *b*, N=1,050 rpm, f=39.2 c/s; curve *c*, N=1,550 rpm, f=47.1 c/s; curve *d*, N=1,960 rpm, f=54.6 c/s; and curve *e*, N=2,250 rpm, f=60.2 c/s.

tip deflection is increased somewhat to compensate for the lessening in curvature and hence in stress in the outboard portion of the blade.

Figure 11 shows the effect of rotation on the stress distribution in the same propeller blade, assuming the hub to be free.

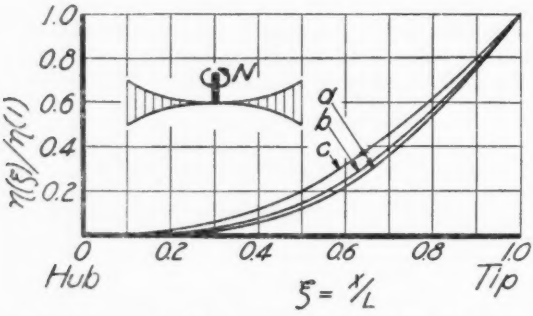

FIGURE 8.—*Deflection curves for fundamental mode of blade type 4371 clamped at center of hub, rotating at a speed N, and vibrating with a frequency f.*

Curve *a*, N=0 rpm, f=26.0 c/s; curve *b*, N=860 rpm, f=32.6 c/s; and curve *c*, N=2,020 rpm, f=50.6 c/s.

Figure 12 shows the effect of rotation on the stress distribution of a blade of type 4371 clamped at the center of the hub. The shape of this blade is such as to lead to two points of maximum stress amplitude.

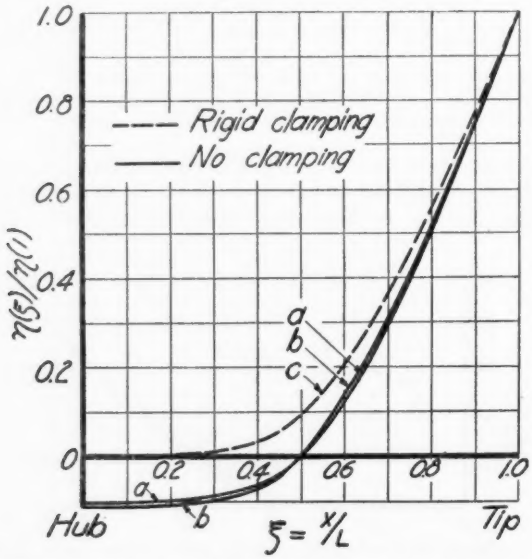

FIGURE 9.—*Deflection curves per inch tip deflection for fundamental mode of blade of type 32 rotating at a speed N and vibrating with a frequency f, but without clamping at center of hub.*

Curve *a*, N=0 rpm, f=34.1 c/s; and curve *b*, N=1,620 rpm, f=55.2 c/s.

Deflection curve per inch tip deflection for nonrotating blade with rigid clamping at center of hub.

Curve *c*, N=0 rpm, f=30.7 c/s.

The first maximum lies at a section 55 percent of the blade length from the hub and predominates at low speeds of rotation, while the second maximum, which is 35 percent of the blade length from the hub, predominates at high speeds of rotation. In spite of a consider-

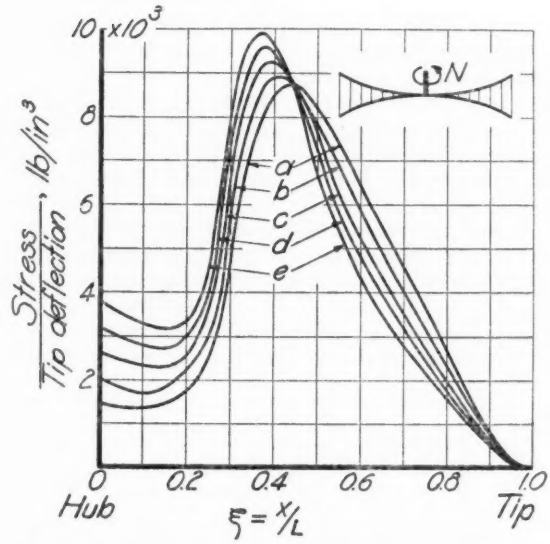

FIGURE 10.—*Extreme fiber stress per inch of tip deflection along the center line on the convex side for the fundamental mode of blade type 32 clamped at center of hub, rotating at a speed N, and vibrating with a frequency f.*

Curve *a*, N=0 rpm, f=30.6 c/s; curve *b*, N=1,050 rpm, f=39.2 c/s; curve *c*, N=1,550 rpm, f=47.1 c/s; curve *d*, N=1,960 rpm, f=54.6 c/s; and curve *e*, N=2,250 rpm, f=60.2 c/s

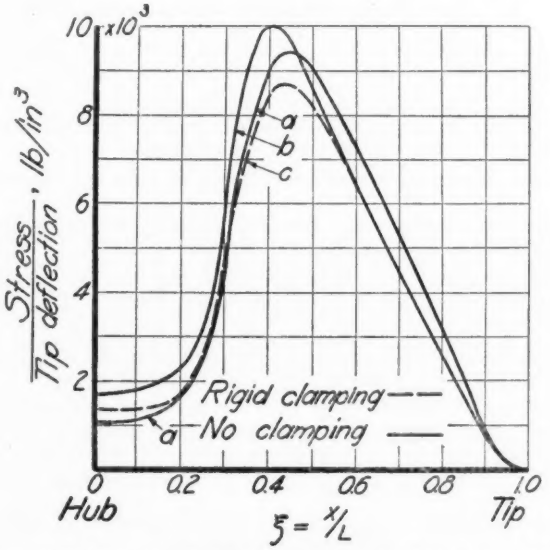

FIGURE 11.—*Stress distribution for fundamental mode of blade type 32 rotating at a speed N and vibrating with a frequency f, but without clamping at center of hub.*

Curve *a*, N=0 rmp, f=34.1 c/s; and curve *b*, N=1,620 rmp, f=55.2 c/s.

Corresponding curve for nonrotating blade with rigid clamping.

Curve *c*, N=0 rpm, f=30.7 c/s.

able change in the shape of the stress-distribution curve, the magnitude of the maximum stress per unit tip deflection is changed less than 13 percent as a result of rotation.

Figures 10, 11, and 12 all lead to the same conclusion, namely, that the effect of speeds of rotation in the operating range (1,000 to 2,000 rpm) on the maximum stress per unit tip deflection for the fundamental flexural mode may be neglected when designing propellers, especially in view of the uncertainty in the value of the tip deflection. It is allowable for approximate calculations to take the resultant stress in the blade as the sum of the static centrifugal-force stress (fig. 6), the static bending stress due to air forces, and a sinusoidally varying stress whose amplitude may be calculated, provided the tip amplitude of the blade is given, by using the same ratio of stress to tip amplitude as that determined either by direct measurement or

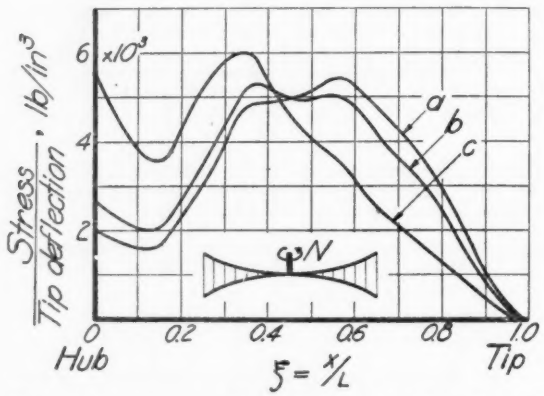

FIGURE 12.—*Extreme fiber stress per inch tip deflection along the center line on the convex side for the fundamental mode of blade type 4371 clamped at center of hub, rotating at a speed N, and vibrating with a frequency f.*

Curve *a*, N=0 rpm, f=26.0 c/s; curve *b*, N=860 rpm, f=32.6 c/s; and curve *c*, N=2,020 rpm, f=50.5 c/s.

by calculation, upon the same blade vibrating with the fundamental flexural mode without rotation.

The preceding statement assumes that the steady air forces have no effect on the vibration of the propeller blade. This assumption is supported by the theoretical work of Reissner [17], who found that the modes of rotating propeller blades are practically unaffected by small initial curvatures such as may be produced by air forces.

If the location of the point of maximum stress is desired the possibility of a considerable shift toward the hub must be considered in those cases (e. g., fig. 12) in which the stress for no rotation decreases slowly on the hub side of the point of maximum stress.

3. MODE OF MOTION AND STRESS DISTRIBUTION FOR SECOND HARMONIC MODE

(a) OUTLINE OF PROCEDURE

The procedure outlined above for calculating the fundamental mode cannot be directly applied to the calculation of one of the harmonic modes. The procedure is a method of iteration in which the

solution generally converges to the fundamental mode. The difficulty may be circumvented, at least for the second harmonic mode [1], by forcing the deflection curve through a nodal point and varying the position of the nodal point until eq 23 or 24 is satisfied for all sections along the vibrating blade. Obviously, this is a very cumbersome procedure and one that can hardly be extended to a calculation of harmonics with more than one nodal point along the blade.

A more convenient and more generally applicable procedure may be derived by eliminating the modes of lower frequency than the desired mode from the assumed mode. The procedure is easily understood if it is realized that the solutions of eq 22 are orthogonal. This may be proved as follows.

Let $\varphi_p(\xi)$, $\varphi_q(\xi)$ be two solutions η of eq 22. They will then satisfy eq 10 independently, and we may write eq 10, first with φ_p in place of η, and then with φ_q in place of η. Multiplying the first one of these equations by φ_q and the second one by φ_p, subtracting one equation from the other, and integrating over the length of the blade gives the following equation:

$$\left.\begin{aligned}(k_p-k_q)\int_0^1 f\varphi_p\varphi_q d\xi=&\int_0^1\left(\varphi_q\frac{d^2i\varphi_p''}{d\xi^2}\phi_p-\frac{d^2i\varphi_q''}{d\xi^2}\right)d\xi\\&-\frac{\rho L^2\omega^2}{E}\int_0^1\left(\frac{\varphi_q du\varphi_p}{d\xi}-\frac{\varphi_p du\varphi_q}{d\xi}\right)d\xi.\end{aligned}\right\}\quad(25)$$

Integrating the terms on the right side of this equation by parts leads to

$$(k_p-k_q)\int_0^1 f\varphi_p\varphi_q d\xi=\left(\varphi_q\frac{di\varphi_p''}{d\xi}-\varphi_p\frac{di\varphi_q''}{d\xi}\right)-(\varphi_q'i\varphi_p''-\varphi_p'i\varphi_q'')$$

$$-\frac{\rho L^2\omega^2}{E}(\varphi_q u\varphi_p'-\varphi_p u\varphi_q')\Bigg|_{\xi=0}^{\xi=1}.\quad(26)$$

The terms on the right of eq 26 disappear for the upper limit $\xi=1$, since the shear force (proportional to $di\varphi''/d\xi$), the bending moment (proportional to $i\varphi''$), and the centrifugal force (proportional to u) must be zero at the tip $\xi=1$. At the lower limit, $\xi=0$, all terms except the first pair disappear because the slope (proportional to φ') is zero at the hub $\xi=0$ for symmetrical modes. The first pair of terms is from eq 18 and 19

$$\left(\varphi_q\frac{di\varphi_p''}{d\xi}-\varphi_p\frac{di\varphi_q''}{d\xi}\right)\Bigg|_{\xi=0}^{\xi=1}=-\left[\varphi_q(0)\left(\frac{di\varphi_p''}{d\xi}\right)_{\xi=0}-\varphi_p(0)\left(\frac{di\varphi_q''}{d\xi}\right)_{\xi=0}\right]$$

$$=-\varphi_q(0)\varphi_p(0)[m(k_p-k_q)-k_ps_p+k_qs_q].\quad(27)$$

From eq 18 and 19 we note that

$$ks=\frac{S}{LE}=\text{constant},\quad(28)$$

so that the last two terms in eq 27 drop out. Substituting the resulting value of eq 27 in eq 26 gives the relation of orthogonality

$$m(\varphi_p\varphi_q)_{\xi=0}+\int_0^1 f\varphi_p\varphi_q d\xi=0,\ p\neq q. \tag{29}$$

The first step in the procedure of solving eq 23 and 24 for harmonic modes consists in obtaining an assumed deflection curve η which satisfies the four boundary conditions, eq 12, 15, and 21. It is possible to express this curve η in terms of the normalized deflection curves[2] $\varphi_1(\xi)$, . . . $\varphi_n(\xi)$ . . . for the natural modes of the propeller blade that are solutions of eq 22:

$$\eta(\xi)=a_1\varphi_1(\xi)+\ \ldots\ +a_n\varphi_n(\xi)+\ \ldots\ . \tag{30}$$

If the right-hand side of eq 30 is substituted in eq 22 and the integration performed, a new curve,

$$I_1=a_1\frac{\varphi_1}{k_1}+a_2\frac{\varphi_2}{k_2}+a_3\frac{\varphi_3}{k_3}+\ \ldots\ , \tag{31}$$

is obtained, in which the lower orders are more predominant than in the original curve η, since the frequency ratio, k, increases rapidly with the order of the mode. The second harmonic frequency, for instance, is roughly three times the fundamental frequency for a typical propeller blade; this leads to a value k_2 about 10 times as large k_1. It is thus understood how, by reiterated integration, η converges to the mode having the lowest frequency.

A general method eliminating all modes below the one to be found consists in evaluating the tip amplitudes a_1, . . . , a_n, . . . of the component modes by first multiplying eq 30 by $f\varphi_1(\xi)$, . . . $f\varphi_n(\xi)$, . . . , integrating, and then making use of the condition of orthogonality, eq 29. This leads to the values

$$\begin{aligned} a_1&=\frac{m\eta(0)\varphi_1(0)+\int_0^1 f\varphi_1(\xi)\eta(\xi)d\xi}{\int_0^1 f\varphi_1{}^2(\xi)d\xi}\\ &\ldots\ldots\ldots\ldots\ldots\ldots\\ a_n&=\frac{m\eta(0)\varphi_n(0)+\int_0^1 f\varphi_n(\xi)\eta(\xi)d\xi}{\int_0^1 f\varphi_n{}^2(\xi)d\xi}. \end{aligned} \tag{32}$$

These equations enable us to free the assumed deflection curve, $\eta(\xi)$, of any component modes whose shape has already been determined. If we know all modes below the n-th mode we may calculate the n-th mode by starting out with a deflection curve from which all lower modes have been eliminated,

$$\eta_1=\eta-a_1\varphi_1\ \cdots\ -a_{n-1}\varphi_{n-1}=a_n\varphi_n+a_{n+1}\varphi_{n+1}\ \cdots\ , \tag{33}$$

[2] A deflection curve, $\varphi_1(\xi)$, . . . $\varphi_n(\xi)$, will be considered as normalized in this discussion if its value at the propeller tip is taken as unity, that is, $\varphi_1(1)=1$, . . . $\varphi_n(1)=1$.

and substituting this deflection curve in the integrand on the right-hand side of eq 22, 23, or 24. Carrying out the integration leads to a deflection curve,

$$I_I = a_n \frac{\varphi_n}{k_n} + a_{n+1} \frac{\varphi_{n+1}}{k_{n+1}} + \cdots, \tag{34}$$

in which the n-th mode is more predominant than in η_I, since the frequency ratio, k, increases rapidly with the order of the mode.

To get a better approximation of the n-th mode, one may normalize I_I by multiplying it by a factor which will make the tip deflection unity, and may then repeat the integration with the resulting deflection curve, η_{II},

$$\eta_{II}(\xi) = I_I(\xi)/I_I(1) \tag{35}$$

until the resulting integral is proportional to the $\eta(\xi)$ in the integrand within the accuracy of the numerical procedure used.

A second method of calculating the harmonic modes is considerably less general than the first method, but possibly more convenient, if only the fundamental need be eliminated.

In the second method we free the assumed deflection curve $\eta(\xi)$ of any component modes whose shape has already been determined after the integration of eq 31. The amplitudes a_3, a_4, . . . will be small compared to a_2, provided that η has approximately the shape of the second harmonic mode. If we let $a_3 = a_4 = \ldots = 0$, we may solve eq 31 for k_2 as follows:

$$k_2 = \frac{a_2\varphi_2}{I_I - \frac{a_1\varphi_1}{k_1}} = \frac{\eta_I - a_1\varphi_1}{I_I - \frac{a_1\varphi_1}{k_1}}. \tag{36}$$

The frequency ratio, k_2, must have the same value for all sections along the blade. All quantities in eq 36 are already known except a_1 and k_2. The amplitude a_1 may, therefore, be evaluated by deriving eq 36 for any two sections of the blade. A number of trials showed that the sections $\xi = 0.45$, $\xi = 0.85$ were particularly suitable. That is, a_1 was evaluated from

$$\frac{\eta_I(0.45) - a_1\varphi_1(0.45)}{I_I(0.45) - \frac{a_1\varphi_1(0.45)}{k_1}} = \frac{\eta_I(0.85) - a_1\varphi_1(0.85)}{I_I(0.85) - \frac{a_1\varphi_1(0.85)}{k_1}}. \tag{37}$$

Solving eq 37 for a_1 gave

$$a_1 = \frac{\eta(0.45)\eta(0.85)\left[\frac{I(0.85)}{\eta(0.85)} - \frac{I(0.45)}{\eta(0.45)}\right]}{\varphi_1(0.45)\left[I(0.85) - \frac{\eta(0.85)}{k_1}\right] - \varphi_1(0.85)\left[I(0.45) - \frac{\eta(0.45)}{k_1}\right]} \tag{38}$$

Knowing a_1, a further approximation to η was obtained from eq 30 by evaluating

$$I_I - a_1 \frac{\varphi_1}{k_1} \tag{39}$$

and normalizing this expression. Repeating with the normalized curve η_{II} proportional to eq 39 gave a still closer approximation η_{III}.

It was found that the fundamental component a_1 was negligible compared with a_2 after the third run; three runs generally sufficed to obtain an accurate solution of eq 23 or 24 for the second harmonic mode.

A check determination of the second harmonic mode of a blade type 4371 rotating at 860 rpm was made to verify that both the procedures outlined above led to the same numerical result.

(b) RESULTS

The second harmonic mode was calculated by the second procedure outlined above for a number of rates of rotation for a blade of type 32

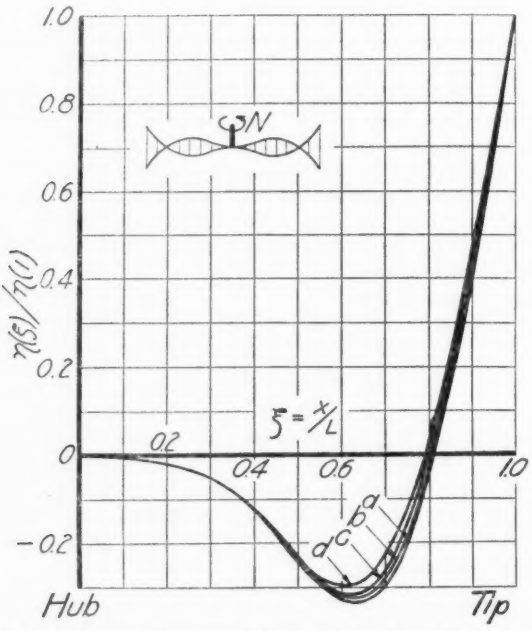

FIGURE 13.—*Deflection curves for second harmonic mode of blade type 32 clamped at center of hub, rotating at a speed N, and vibrating with a frequency f.*

Curve *a*, N=0 rpm, f=119 c/s; curve *b*, N=814 rpm, f=124 c/s; curve *c*, N=1,210 rpm, f=131 c/s; and curve *d*, N=2,240 rpm, f=153 c/s.

clamped at the center of the hub. The results are shown in figures 13 and 14.

Figure 13 gives the shape of the mode for rates of rotation from 0 to 2,240 rpm. The deflection is seen to change only slightly because of rotation.

The effect of the rotation on the stress distribution is shown in figure 14. Comparison of this figure with figure 10 shows that the effect of rotation on the stress distribution is less than for the fundamental mode.

The effect of rotation on the natural modes may, in general, be expected to decrease with increased orders of vibration. In the higher orders practically all the energy stored in the deflected posi-

tion is energy of bending and the proportion of restoring force due to rotation becomes small compared with that due to bending. It may be concluded that except for the fundamental mode the stress distribution for a given tip deflection of a rotating blade vibrating with a flexural mode may be approximated closely by superimposing the vibratory stress in that mode, as determined for no rotation on the static stresses due to centrifugal force and to air loads.

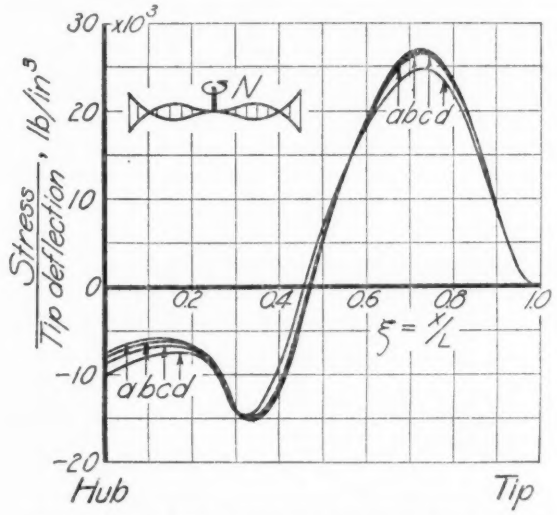

FIGURE 14.—*Extreme fiber stress per inch tip deflection along the center line on the convex side for the second harmonic mode of blade type 32 clamped at center of hub, rotating at a speed N, and vibrating with a frequency f.*

Curve *a*, N=0 rpm; f=119 c/s; curve *b*, N=814 rpm, f=124 c/s; curve *c*, N=1,210 rpm, f=131 c/s; and curve *d*, N=2,240 rpm, f=153 c/s.

III. CALCULATION OF NATURAL FREQUENCIES

An accurate knowledge of the natural frequencies of vibration of a propeller blade is required whenever there is a possibility of resonance between the propeller vibration and a periodic exciting force of sufficient amplitude from the engine. Accurate values of the frequency for the extreme end conditions of rigid clamping and of no clamping at the hub can be obtained by solving the integral eq 23 and 24, as was shown above. This involves too much calculation for practical design and fortunately is not necessary for speeds of rotation of a practical order.

1. APPROXIMATE CALCULATION BY RAYLEIGH'S METHOD

For speeds of rotation of a practical order, the shape of the deflection curve is not changed appreciably by the centrifugal force, and an accurate value of the natural frequency may be obtained, as noted below, by the Rayleigh energy method [10].

Rayleigh's method determines the natural frequency for a given mode $X(x)$ of an elastic system from the equality of the potential energy, V, stored in the system at the extreme position and the kinetic

energy, T, acquired by the system when it swings through its mean position. The potential energy of a rotating straight bar of variable section vibrating transversely consists of two terms [12]: (1), the potential energy due to bending,

$$V'=\frac{E}{2}\int_0^L I\left(\frac{d^2X}{dx^2}\right)^2 dx; \tag{40}$$

and (2), the potential energy V'' due to the inward motion of the particles in the blade against centrifugal force.

$$V''=\int_0^L\left[\omega^2\rho Ax\int_0^x\frac{1}{2}\left(\frac{dX}{dx}\right)^2 dx\right]dx. \tag{41}$$

The kinetic energy for sinusoidal vibrations, as given by eq 7, will be

$$T=\frac{p^2}{2}\int_0^L\rho AX^2dx. \tag{42}$$

The integrals on the right-hand side of eq 40 to 42 may be written more conveniently in terms of the ratios in eq 9. Doing this, and substituting the resulting expressions in the condition of conservation of energy,

$$V'+V''=T, \tag{43}$$

gives the following values for the square of the natural frequency, p, in radians per second:

$$p^2=\frac{\dfrac{E}{\rho L^2}\displaystyle\int_0^1 i\eta''^2d\xi+\omega^2\int_0^1\left[f\xi\int_0^\xi\eta'^2d\xi\right]d\xi}{\displaystyle\int_0^1 f\eta^2d\xi}. \tag{44}$$

Equation 44 may be written in the form of the well-known eq 1,

$$p^2=p_0^2+\alpha\omega^2(\text{rad/sec})^2, \tag{45}$$

where

$$p_0^2=\frac{\dfrac{E}{\rho L^2}\displaystyle\int_0^1 i\eta''^2d\xi}{\displaystyle\int_0^1 f\eta^2d\xi};\ \alpha=\frac{\displaystyle\int_0^1\left[f\xi\int_0^\xi\eta'^2d\xi\right]d\xi}{\displaystyle\int_0^1 f\eta^2d\xi} \tag{46), (47}$$

provided η is taken as proportional to the deflection curve for no rotation.

The quantity p_0^2 will be the square of the frequency without rotation and the ratio α will be constant as long as the shape $\eta''(\xi)/\eta(1)$ of the curvature curve, the shape $\eta'(\xi)/\eta(1)$ of the slope curve, and the shape $\eta(\xi)/\eta(1)$ of the deflection curve remain unaffected by the rotation ω. The detailed analysis of the previous section showed that this is approx-

imately the case for propellers of usual design rotating at service speeds.

The closeness with which Rayleigh's method will give the correct solution of eq 23 and 24 for the fundamental frequency of a propeller blade, provided the mode for no rotation is substituted for η, is brought out by a comparison of curves (*a*) and (*b*) in figure 15 (*A*) and 15 (*B*) with the open circles which were calculated for a blade of type 32 by direct solution of eq 23 and 24.

The insensitiveness of Rayleigh's method to variations in the shape of the deflection curve is so great that the deflection curve, η, for a vibrating beam is frequently approximated by the deflection curve of the beam under its own weight. The deflection curve of the propeller blade as a cantilever beam deflected by its own weight follows from eq 23 by letting $\omega=0$ and by replacing the vibrational acceleration, $p^2X=Lp^2\eta$, by the acceleration of gravity, g. Curve *c* in figures

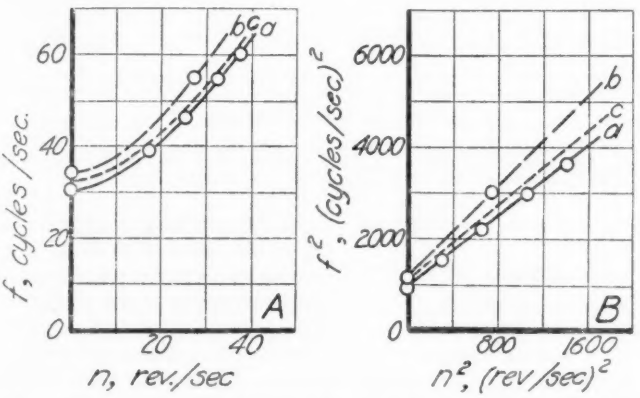

FIGURE 15.—*Variation of natural frequency, f, of fundamental mode with speed of rotation, n, for blade type 32.*

The points were calculated by solving integral equations 23 and 24, respectively.
Curve *a*, Rayleigh's method using the mode for no rotation of a fixed-free blade, $f^2=30.9^2+1.95n^2$ (c/s)²; curve *b*, Rayleigh's method using the mode for no rotation of a free-free blade, $f^2=34.1^2+2.46n^2$ (c/s)²; and curve *c*, Rayleigh's method using the deflection curve of the blade under its own weight, $f^2=32.7^2+2.04n^2$ (c/s)².

15 (*A*) and 15 (*B*) results for a blade of type 32. It is seen that the error in frequency as given by this procedure may be as much as 5 percent in this particular case.

The exactness with which the linear relation eq 45, between $p^2=(2\pi f)^2$ and $\omega^2=(2\pi n)^2$ holds is brought out in the plot of f^2 against n^2 in figure 15 (*B*).

It may be concluded that eq 45 will give an excellent approximation to the natural frequencies of a rotating blade for ordinary values of ω, provided p_0 is either directly observed or is calculated by the relatively exact method [1, 7] for no rotation. The ratio α may then be calculated by substituting the deflection curve, $\eta(\xi)$, for no rotation in eq 47. It may be expected to vary with a change in the design of the blade which would change the shape of the deflection curve, $\eta(\xi)$, or the weight distribution, f.

2. RESULTS FOR FUNDAMENTAL FREQUENCY AND SECOND HARMONIC FREQUENCY

Rayleigh's method, using the shape of the natural mode for no rotation, was applied to calculate the fundamental frequency and the second harmonic frequency of propeller blades of type 32 and type 4371 for the two extreme end conditions of rigid clamping (zero deflection, zero slope) at the hub and complete freedom (zero slope, zero shear) at the hub. The results are listed in table 1 and are shown as curves in figure 16 (*A*) and 16 (*B*) for a blade of type 32 and in figure 17 for a blade of type 4371. The open circles in the figures indicate the results of solving eq 23 and 24 for the natural mode. The solid points in figure 17 are the results of experimental observations made by Theodorsen on a model blade of type 4371 [9], which results were communicated to the authors of the present paper by letter.

The open circles for the "exact" solution are seen to check the curves calculated from Rayleigh's method within the computational error. The solid points obtained by Theodorsen lie inside the narrow band bounded by the curves for the fixed-free and the free-free end conditions.

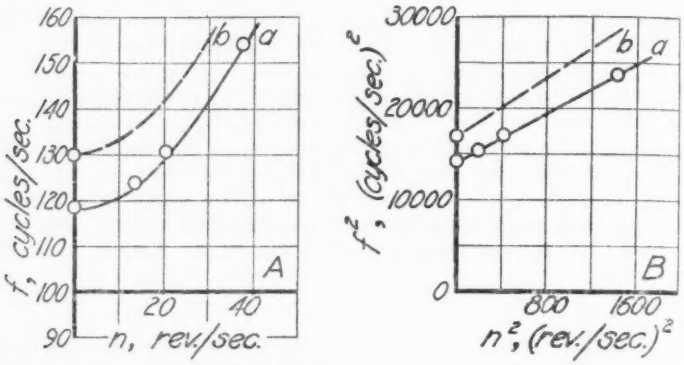

FIGURE 16.—*Variation of natural frequency, f, of second harmonic mode with speed of rotation, n, for blade type 32.*

The points were calculated by solving integral equations 23 and 24, respectively. Curve *a*, Rayleigh's method using the mode for no rotation of a fixed-free blade, $f^2=117.5^2+6.8n^2$ (c/s)^2; and curve *b*, Rayleigh's method using the mode for no rotation of a free-free blade, $f^2=130^2+8.0n^2$ (c/s)^2.

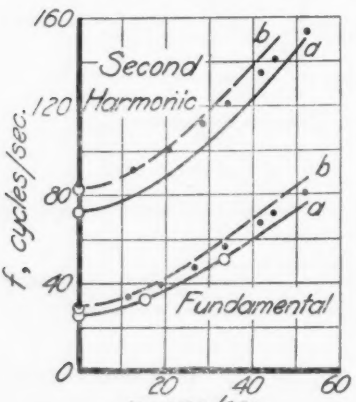

FIGURE 17.—*Variation of fundamental and second harmonic frequencies, f, with speed of rotation, n, for blade type 4371.*

The open points were calculated by solving integral equations 23 and 24, respectively. Curve *a*, Rayleigh's method using the mode for no rotation of a fixed-free blade, fundamental mode, $f^2=26.2^2+1.85n^2$ (c/s)^2 and second harmonic mode, $f^2=72.4^2+6.45n^2$ (c/s)^2; curve *b*, Rayleigh's method using the mode for no rotation of a free-free blade, fundamental mode, $f^2=29.5^2+2.50n^2$ (c/s)^2, and second harmonic mode, $f^2=83.2^2+7.73n^2$ (c/s)^2. The closed points were values derived by Theodorsen from experiments with an affine model (one-tenth thickness) of blade type 4371.

TABLE 1.—*Variation of natural frequency, f, with speed of rotation, n, for blades of two types*

Type of blade	Method of determining frequency	End condition	Mode	Frequency, f
				c/s
32	Rayleigh [1]	Fixed-free	Fundamental	$(30.9^2+1.95n^2)^{\frac{1}{2}}$
32	do.[1]	Free-free	do	$(34.1^2+2.46n^2)^{\frac{1}{2}}$
32	do.[1]	Fixed-free	Second harmonic [2]	$(117.5^2+6.8n^2)^{\frac{1}{2}}$
32	do.[1]	Free-free	do.[2]	$(130^2+8.0n^2)^{\frac{1}{2}}$
4371	do.[1]	Fixed-free	Fundamental	$(26.2^2+1.85n^2)^{\frac{1}{2}}$
4371	do.[1]	Free-free	do	$(29.5^2+2.50n^2)^{\frac{1}{2}}$
4371	do.[1]	Fixed-free	Second harmonic [2]	$(72.4^2+6.45n^2)^{\frac{1}{2}}$
4371	do.[1]	Free-free	do.[2]	$(83.2^2+7.73n^2)^{\frac{1}{2}}$
4371	From model blade [3]	Unknown	Fundamental	$(30^2+2.05n^2)^{\frac{1}{2}}$
4371	do.[3]	do	Second harmonic [2]	$(84.1^2+6.07n^2)^{\frac{1}{2}}$

[1] Using shape of natural mode for no rotation.
[2] Mode having one node near tip of blade.
[3] Test results by Theodorsen on model blade having one-tenth the thickness of prototype 4371.

3. EFFECT OF RESTRAINT AT HUB; CORRECTION TO RP764 [1]

Examination of table 1 and of figures 15 to 17 shows that a change in the condition of restraint of the blade at the hub may change the natural frequency of the flexural vibrations by as much as 13 percent. The natural frequency for the free-free end condition is 10 to 13 percent higher than that for the fixed-free end condition for blades of both type 32 and 4371.

An effect of restraint on frequency not considered in figures 15 to 17 is that due to the finite length of the hub clamp. This will be equivalent to a shortening of the blade or to a displacement of the point of clamping toward the tip. Calculations for a nonrotating blade of type 32, whose point of clamping was moved as much as 15 percent of the blade length toward the tip, gave an increase of 2 percent for the fundamental frequency as compared with the frequency for clamping at the center of the hub and an increase of 7 percent in the second harmonic frequency. The effect was too small to make it worth-while to extend the calculation to rotating blades. It appears, furthermore, that the direction of the effect is such as to increase the frequency for the clamped-free end condition so that the frequencies of blades with finite hub-clamps may be expected to lie inside the theoretical bands given in figures 15 to 17. An experimental confirmation of this result is desirable, especially in view of the limitation of the theoretical work (see p. 644) to symmetrical modes with a restraint at the hub which may be replaced by a concentrated mass without any spring.

The statement made above that the natural frequency of a propeller blade increases as the point of clamping is moved toward the tip, calls for a correction of results to the opposite effect cited on p. 205, 208, and 209 of [1]. An error was found in the calculation for the frequencies cited on these pages for a blade of type 32 clamped at a point removed from the center of the hub. Correcting this error showed that a displacement of the point of clamping equal to 15 per-

cent of the blade length raised the frequency for the fundamental from 30.7 to 31.3 c/s and that of the second harmonic mode from 116.8 to 125.0 c/s. A displacement of 5 percent in the point of clamping raised the frequency of the second harmonic mode from 116.8 to 121.8 c/s. After making these corrections it may be concluded that the resultant variation in frequency will lie inside the 13 percent range limited by the frequencies for the fixed-free and free-free end condition. This range is comparable to the variation of about 10 percent that was found in the maximum stress per unit tip deflection for different conditions of restraint.

4. EFFECT OF INITIAL TWIST AND OF INITIAL CURVATURE

The expression, eq 44, was derived for a straight propeller blade without initial twist or initial curvature. Actual propeller blades always show a large initial twist and a small amount of initial curvature. Reissner [17] concluded from his theory of twisted and curved propeller blades that the initial curvature had a small effect, while the initial twist may have a considerable effect on the natural frequencies of a rotating blade vibrating flexurally. He derived expressions corresponding to eq 40, 41, and 42 for the potential energy and the kinetic energy of a twisted and curved blade vibrating flexurally while in rotation. These expressions show that a change in the angle of attack of the blade as a whole has no effect on p_0; a twist varying along the blade has a certain effect. The smallness of the effect of initial twist on the fundamental mode and second harmonic mode of a nonrotating blade is indicated by the good agreement between the frequencies and stresses calculated for the straight blade and those measured for an actual twisted blade [1]. The smallness of the effect on the coefficient α occurring in eq 45 is shown by the close agreement between the calculated frequencies of the first two modes and those determined experimentally by Theodorsen on a model of a blade of type 4371. The principal axes of this blade twisted through approximately 35° in passing from a section 8 inches from the center of the hub to a section 56 inches from the center of the hub. It may be concluded that the effect of twist on the fundamental and second harmonic frequency of a propeller blade of this design is small compared to the effect of end restraint at the hub.

5. CRITICAL SPEEDS

Curves of natural frequency versus speed of rotation, such as figures 16 and 17, may be used to estimate the critical speeds of rotation of the propeller, that is, those speeds at which there may be resonance between periodic impulses acting on the propeller with one of the natural frequencies of the propeller system. A condition of resonance is required to set up sufficiently high stresses in the propeller blades to cause their failure by fatigue.

The frequency of the exciting forces acting on a propeller in flight will in general be proportional to the speed of rotation of the propeller. They will be represented by straight lines through the origin, such as are shown in figures 18 and 19. The intersection of these straight lines with the bands denoting the natural frequencies gives the regions within which one may expect a critical speed.

The straight lines in figures 18 and 19 were drawn to illustrate the determination of critical speeds leading to flexural vibrations in the fundamental mode and the second harmonic mode for blades of types 32 and 4371.

Line *a* corresponds to exciting forces of the rotational frequency of the propeller, such as may be set up by a primary unbalance in the rotating system, or an asymmetry in the setting of one of the propeller blades which would cause a disturbance of propeller-rotation frequency in the airflow. This line does not intersect any of the blade-frequency curves since the blade frequency, f, is always higher than the frequency of rotation, n, due to the finite flexural rigidity of the blade.

Line *b* corresponds to exciting forces having twice the rotational frequency of the propeller. Such excitation may exist in a two-blade

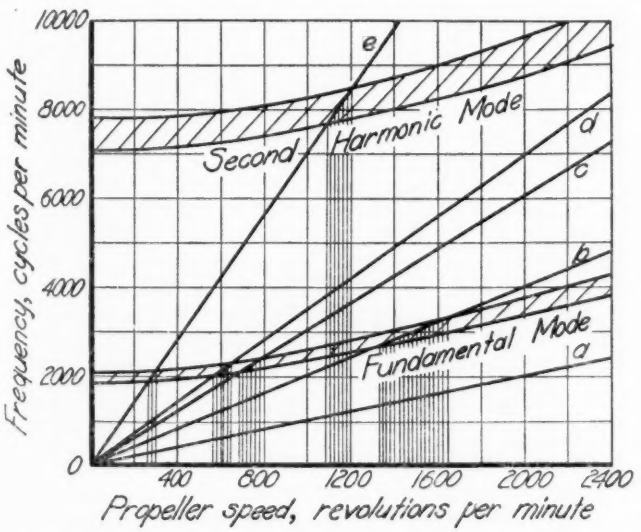

FIGURE 18.—*Critical speeds for flexural vibrations with fundamental mode and second harmonic mode, blade type 32.*

Curve *a*, $f=n$; curve *b*, $f=2n$; curve *c*, $f=3n$; curve *d*, $f=3.5n$; and curve *e*, $f=7n$.

propeller in which each tip passes close to a part of the airplane structure once per revolution. An exciting couple of twice the frequency of rotation will act on a two-blade propeller of an airplane flying in a curved path due to the gyroscopic couple [13] required to change the direction of the angular momentum of the propeller-engine combination during the turn.

Line *c* may enter in a three-blade propeller in which each tip passes once during a revolution close to a structural part of the airplane.

Line *d* corresponds to the principal variation in the gas-pressure torque (3½ times per revolution) for a single-row seven-cylinder engine with direct drive.

Line *e* corresponds to the principal variation in the gas-pressure torque (7 times per revolution) for a double-row 14-cylinder engine with direct drive.

In geared engines one would have to multiply the frequency of the unbalanced torque components in the engine by the gear ratio to obtain the frequency of the torque pulsations acting on the propeller hub.

The regions within which a critical speed may lie which leads to flexural vibrations in the fundamental mode or the second harmonic mode, are indicated by vertical shading. In the case of a blade of type 32, figure 18 indicates two dangerous regions for propellers rotating between 1,000 and 2,000 rpm. Unbalanced torques from the individual cylinders in a double-row 14-cylinder engine may lead to a resonant tip vibration at a speed somewhere between 1,080 and 1,200 rpm. Torque variations of the second order may excite resonant

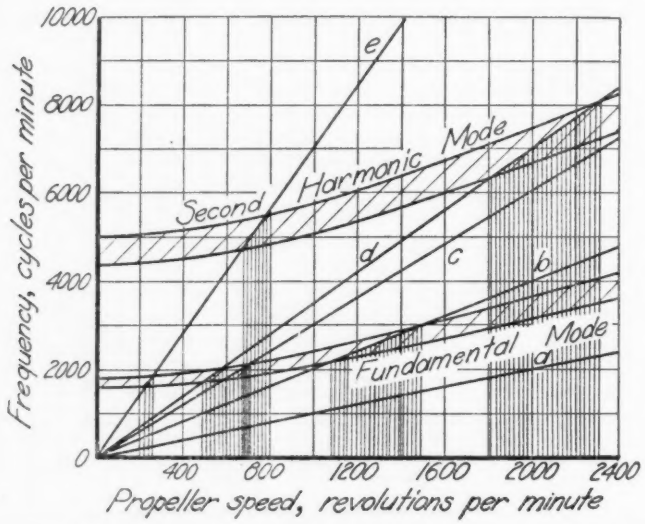

FIGURE 19.—*Critical speeds for flexural vibrations with fundamental mode and second harmonic mode, blade type 4371.*

Curve *a*, $f=n$; curve *b*, $f=2n$; curve *c*, $f=3n$; curve *d*, $f=3.5n$; and curve *e*, $f=7n$.

vibrations in the fundamental mode somewhere between 1,340 and 1,640 rpm.

In the case of a blade of type 4371, figure 19 indicates two dangerous regions for propellers rotating between 1,000 and 2,000 rpm. Resonant vibrations in the fundamental mode may be excited by second order torque variations at a speed somewhere between 1,080 and 1,500 rpm. Resonant tip vibrations may be excited by 3½-order torque variations due to the firing in the individual cylinders of a single-row seven-cylinder engine at a speed somewhere between 1,800 and 2,300 rpm.

It should be emphasized that the above discussion is only intended as an illustrative example, and that it does not give a complete picture of all possible critical speeds that may be expected in a propeller of the type 32 and type 4371. Figures 18 and 19 do not contain the higher harmonics of flexural vibration which may be the cause of some tip failures in service [14]. Another omission is that mode in which the

propeller vibrates as a torsion pendulum with the crankshaft as elastic member. Its frequency in this mode may be calculated by well-established methods [15]; it is nearly independent of the speed of rotation and will, therefore, be represented as a horizontal straight line in figures 18 and 19. Another mode that may be important in some cases is the torsional mode of the blade about its longitudinal axis. The frequency of this mode will be very high for all except very thin blades, such as solid-steel propeller blades.

A further limitation which must be kept in mind in applying diagrams of the type of figures 18 and 19 is that they neglect the coupling between different modes of vibration. The effect of coupling between the flexural vibrations of a propeller blade and the torsional vibration of the propeller about the crankshaft has been investigated for certain idealized cases by Carter [16].

In spite of all the limitations to which the diagrams in figures 18 and 19 are subject, their introduction may serve a useful purpose in pointing out the possibility of a large uncertainty in the critical speed corresponding to a small uncertainty in the natural frequencies of a propeller. If all natural modes of vibrations were included in the figures, it is probable that only a small portion of the service range of speeds would lie outside the possibility of resonance.

One will always have to contend with the presence of one or more critical speeds somewhere in the service range. It would be of some help if the location of these critical speeds could be determined much more accurately by experiment or otherwise than is possible with a chart such as figures 18 or 19, but it would be far better if the intensity of the periodic exciting forces acting on the propeller were reduced so that the stresses set up at a critical speed would lie below the endurance limit of the material. Adequate vibration insulation of the engine from the propeller would, for instance, reduce the excitation corresponding to curves e and d in figures 18 and 19 to a low figure and may prevent fatigue failures due to tip vibration in the second harmonic mode.

IV. COMPARISON OF NATURAL MODES FOR AFFINE PROPELLER BLADES

The work involved in obtaining a solution for a natural flexural mode of a given propeller blade is too great for routine calculation. Complete solutions will probably be carried out for only a few characteristic types of propeller blades. This makes it important to find a model rule which would permit application of these particular solutions to propeller blades of other materials and of shapes that are affine [3] to the shape of one of the propeller blades that has been studied in detail.

A model rule for predicting the natural frequencies of a given propeller blade from the frequency of a propeller blade of affine shape has already been stated and applied by Theodorsen [9]. Theodorsen

[3] Two propeller blades, 1 and 2, are considered to be affine in shape if the surface $f_1(x_1, y_1, z_1)=0$ of the first blade may be transformed to the surface $f_2(x_2, y_2, z_2)=0$ of the second by a linear transformation of the coordinates such that for corresponding points $x_2=\alpha x_1$, $y_2=\beta y_1$, $z_2=\gamma z_1$, where α, β, γ are constants. This may be expressed more concisely in mathematical terms by stating that the two surfaces may be written in the form $f(x, y, z)=0$ and $f(\alpha x, \beta y, \gamma z)=0$, where α, β, γ are constants.

states that the frequency of a given mode of flexural vibration of similar propeller blades will vary as the ratio

$$\frac{DV_s}{L^2}, \tag{48}$$

where L is the length of the blade, D is a quantity representative of the thickness, say the diameter of the blade at the hub, and $V_s=(E/\rho)^{1/2}$ is the velocity of longitudinal sound vibrations in the blade material.

For rotating propellers, Theodorsen derived the following model rule by proceeding from the frequency equation, eq 1. "The relative increase in frequency due to centrifugal force in similar [4] propellers is the same for the same value of the quantity

$$\frac{DV_s}{LV_T}, \tag{49}$$

where V_T is the tip velocity of the propeller." The use of the approximate relation eq 1 as a proof for eq 49 is permissible in view of the excellent agreement between eq 1 and the more exact solution (see fig. 16 and 17).

The model rules in eq 48 and 49 were derived for the flexural frequencies of propeller blades only. It is not safe, without further investigation, to conclude that they will give the conditions under which the flexural modes and hence the stress-distributions of two affine propellers are the same. An answer to this question for the idealized straight propeller blades, at least (see p. 641), may be obtained by determining under what conditions the deflection curves $X_1(x_1)$ and $X_2(x_2)$ of two affine propellers satisfy the same differential equation, 8 or 10. If X_1 and X_2 satisfy the same equation at all points along the two propeller blades and if the conditions of restraint are the same, X_1 and X_2 must be proportional to each other according to eq 8 and the deflection curves and stress-distribution curves must be the same for the two blades.

Let α, β, γ be the ratios of affinity for length, breadth, and thickness dimensions of the two affine propeller blades, that is,

$$\alpha=L_2/L_1,\ \beta=b_2/b_1,\ \gamma=c_2/c_1, \tag{50}$$

where L is the length of the blade and b and c are respectively the breadth and thickness of the blade at a section a given percentage of the blade length from the tip. The subscripts 1 and 2 refer to the blades 1 and 2 that are being compared. The condition that the deflection curves $\eta_1=X_1/L_1$, and $\eta_2=X_2/L_2$ of the two blades satisfy the same differential equation, eq 10, is expressed by

$$\frac{d^2}{d\xi_2^2}i_2\eta_2''-k_2\left[f_2\eta_2+\left(\frac{\omega_2^2}{p_2^2}\right)\frac{d}{d\xi_2}u_2\eta_2'\right]=\frac{d^2}{d\xi_1^2}i_1\eta_1''-k_1\left[f_1\eta_1+\left(\frac{\omega_1^2}{p_1^2}\right)\frac{d}{d\xi_1}u_1\eta_1'\right]. \tag{51}$$

The ratios ξ_1, ξ_2, i_1, i_2, . . . are, according to eq 9 and 50, related by

$$\xi_2=\xi_1,\ f_2=\frac{\beta\gamma}{\alpha^2}f_1,\ i_2=\frac{\beta\gamma^3}{\alpha^4}i_1,\ k_2=\alpha^2\left(\frac{p_2}{p_1}\frac{V_{s1}}{V_{s2}}\right)^2k_1,\ u_2=\frac{\beta\gamma}{\alpha^2}u_1. \tag{52}$$

[4] Theodorsen uses the word "similar" in [9] in place of the term "affine" used in this paper.

The substitution of eq 52 in eq 51 shows that eq 51 is satisfied if

$$\eta_1=\eta_2;\ \frac{\alpha^4}{\gamma^2}\left(\frac{\omega_2}{\omega_1}\frac{V_{s1}}{V_{s2}}\right)^2=1;\ \frac{\alpha^4}{\gamma^2}\left(\frac{p_2}{p_1}\frac{V_{s1}}{V_{s2}}\right)^2=1.$$

These model rules may be written in the more convenient form:

$$\eta_1=\eta_2;\ \frac{\omega_2}{\omega_1}=\frac{p_2}{p_1};\ \frac{p_2}{p_1}=\frac{\gamma}{\alpha^2}\frac{V_{s2}}{V_{s1}}. \tag{53}$$

The last equation is another statement of the model rule eq 48 that had already been given by Theodorsen for nonrotating propellers. Combining the second and third equations in eq 53, and noting that the tip speed, $V_T=L\omega$, leads to Theodorsen's model rule, eq 49, for the relative rise in frequency due to rotation.

It may be concluded that Theodorsen's model rules, eq 48 and 49, can be applied to calculate not only the frequency but also the shape of a natural flexural mode and hence the stress distribution of any idealized straight propeller blade from the corresponding natural mode of a "standard" propeller blade whose length, breadth, and thickness dimensions are affine to those of the propeller blade in question.

Although Theodorsen's model rules were derived for idealized straight blades only, they are probably also applicable to actual twisted blades vibrating with low-frequency flexural modes, in view of the agreement found between the observed stress distribution in a nonrotating blade and that calculated for the corresponding idealized straight blade [1], and in view of the agreement found between the frequencies observed by Theodorsen on a model of blade type 4371 and those calculated for the corresponding idealized straight blade (fig. 17).

An experimental investigation of the natural frequencies and the stress distributions in a rotating propeller blade vibrating in resonance with one of the flexural modes is highly desirable as a check on these conclusions as well as on the other theoretical results presented in this paper.

V. SUMMARY

The procedure for calculating the natural modes of flexural vibration of nonrotating propeller blades, which is described in RP764 has been extended to include the effect of rotation. The integral equations for the symmetrical modes of vibration of an idealized straight blade are given, in particular, for the cases of rigid clamping at the hub and zero clamping at the hub. These equations were solved numerically for aluminum-alloy propeller blades of two typical designs designated as type 32 and type 4371 rotating at speeds which cover the range of service speeds and vibrating with the fundamental flexural mode and with the second harmonic flexural mode (with a node near the tip).

The effect of rotation in the operating range (1,000 to 2,000 rpm) on the maximum stress amplitude per unit tip deflection for the fundamental mode was not more than 13 percent. It is sufficient for approximate calculations to take the resultant stress in a rotating blade vibrating with a given tip amplitude as the sum of the static stress due to centrifugal force and steady air forces and a sinusoidally varying stress whose amplitude is equal to that for the fundamental of the same blade vibrating without rotation with the given tip amplitude.

Application of the same procedure to the second harmonic mode leads to a still better approximation because of the decrease in the relative importance of centrifugal force at the higher flexural modes. There may be a shift towards the hub of as much as 20 percent of the blade length in the location of the point of maximum stress amplitude in those cases in which the stress for no rotation decreases slowly on the hub side of the point of maximum stress amplitude.

The natural frequencies of a rotating propeller blade vibrating flexurally can be calculated by solving the integral equations. This is usually too cumbersome for practice and it is unnecessary since an excellent and convenient approximation to the frequencies obtained in this manner follows from Rayleigh's method by substituting the deflection curve of the propeller blade for no rotation in the expressions for potential and kinetic energy. Rayleigh's method was used to calculate the natural frequencies of the fundamental mode and the second harmonic mode for both types of propeller blades and for the two end conditions of rigid clamping and no clamping at the center of the hub. The frequency of the two flexural modes was found to change 9 to 13 percent in passing from no clamping to rigid clamping. Observed values of natural frequency for the fundamental mode and the second harmonic mode of a model blade of type 4371 which were obtained by Theodorsen at the Langley Memorial Laboratory were found to lie inside the narrow band bounded by the curves for rigid clamping and no clamping.

A displacement of the point of clamping from the center of the hub toward the tip such as may be expected due to the finite length of hub clamp will slightly increase the natural frequency of flexural vibrations. This calls for a correction to RP764 [1], where the opposite conclusion had been reached due to computational error.

The natural frequencies determined by Rayleigh's method may be used to calculate the critical speeds for flexural vibration. Unfortunately, it appears that a given error in the natural frequency of the blade may introduce several times that error in the critical speed, so that the calculated regions containing a critical speed may cover a considerable range of speeds.

Both the natural frequencies for flexural vibration and the stress distribution of a given idealized straight propeller blade may be obtained from the observed frequencies and stress distributions of a model blade that is affine to the blade in question by making use of the two model relations which were first applied by Theodorsen to calculate the frequencies of a propeller blade of type 4371 from a model blade having the same length and width dimensions but having one-tenth the thickness of the prototype.

The above results are based upon theoretical reasoning and hence upon certain idealizing assumptions that can only be realized approximately in an actual propeller blade in flight. An experimental investigation of the natural frequencies and the stress distributions in a rotating propeller blade vibrating in resonance with one of the flexural modes is highly desirable as a check on these predictions of the theory and to establish the modes of vibration which are actually important in setting up severe alternating stresses in a propeller. More experiments are needed to determine the effects of twist on the natural flexural modes; existing tests have shown this effect to be small only for two nonrotating blades and for the fundamental and second

harmonic frequencies of one rotating model blade. Experiment only can give the actual amplitudes of the resonant vibrations; the theory may be of assistance in deducing the amplitude of stresses throughout the blade from the vibration amplitude measured at a convenient point. The carbon resistance strain pick-ups recently developed by A. V. deForest at the Massachusetts Institute of Technology may make an adequate experimental study of propeller vibration possible in the near future.

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EFFECT OF FILLING AND SIZING MATERIALS ON STABILITY OF BOOK PAPERS

By Merle B. Shaw and Martin J. O'Leary

ABSTRACT

The National Bureau of Standards has been carrying on research on the manufacture of papers to obtain information on composition and processes which have an important bearing on the stability of paper. Several publications have been issued as a result of these investigations. Three of them, Research Papers RP372, RP574, and RP794, present data for writing papers. Another Research Paper, RP949, reports the results on experimental unsized papers made from pulps commonly used in book papers. The present publication is an extension of the work on book paper, and relates primarily to the effect of filling and sizing variables introduced in manufacture.

The papermaking materials used were representative commercial products. Four types of fillers, including both natural materials and manufactured pigments, were used. They comprised one clay filler; two titanium dioxide pigments; two zinc sulfide pigments; and two calcium carbonates, one precipitated, the other a natural product, water-ground. The sizing agent, rosin soap prepared from rosin and soda ash, was precipitated by means of papermaker's alum, aluminum sulfate. The fibrous materials covered the range of those commonly used in the fine printing papers. They consisted of sulfite pulp and soda pulp of the ordinary book-paper grade; three "purified" wood pulps, produced by special cooking and bleaching treatments to obtain high purity and strength; new rags, the grade known commercially as No. 1 white shirt cuttings; and two grades of old rags, No. 1 old whites and "twos and blues."

Seventy-two experimental papers were manufactured in the Bureau's semicommercial mill. The papers were given extensive physical and chemical tests with particular reference to stability, both before and after an accelerated aging test made by heating the paper for 72 hours at 100° C.

The strength of the experimental papers decreased with increasing filler content, and was influenced by the amount, not the type, of filler present. There was no pronounced difference in the relative effect of the nonalkaline fillers on sizing. The nonalkaline fillers had less effect than calcium carbonate in reducing the degree of sizing. Although the sizing values of the carbonate-filled papers were not high, the papers were sized sufficiently to be written on with ink and for ordinary printing processes. Maximum clay retention was obtained in the purified wood and the rag papers when the pH at the head box was approximately 5, and decreased as the amount of alum was increased. For the sulfite-soda stock, retention of all the nonalkaline fillers increased as alum was increased. The papers containing titanium dioxide, zinc sulfide, or precipitated calcium carbonate pigments had the highest opacity. Preliminary printing tests made on a few of the filled papers indicated satisfactory printing quality.

The rag and purified wood-pulp papers were more stable to the heat test than the sulfite-soda. Nonalkaline fillers had no apparent harmful influence on the stability of any of the papers, and the calcium carbonate pigments had a protective or inhibiting effect in the aging test.

Acidity was an important factor in deterioration. The attack on the cellulose was increased as the amount of alum was increased, in either the unsized or the rosin-sized papers.

The effect of increasing the amount of alum in the beater and then neutralizing part of the alum with sodium carbonate as the stock was being pumped from

the beater chest to the machine chest was practically the same as having had the final pH value originally in the beater and maintained throughout the preparation of the stock.

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I. INTRODUCTION

As a part of its program of research relating to the stability of papers used for records, the National Bureau of Standards is making a study of the relation of papermaking materials and processes to the strength, stability, and other properties of book papers. This publication is the fifth in the series planned to include the more important types of fibrous and nonfibrous raw materials commonly used in the manufacture of record papers. Of the preceding publications, three [1, 2, 3] [1] related to writing papers and one [4] to fibers commonly found in book papers. The present publication is an extension of the work on book papers and deals primarily with the effect of filling and sizing materials on their stability.

II. PAPERMAKING RAW MATERIALS

The fillers selected were representative of several types, both natural materials and manufactured pigments, and were used as supplied by the manufacturers. They comprised one clay; two titanium pigments,

[1] Figures in brackets indicate the literature references at the end of this paper.

titanium dioxide and a composite of titanium dioxide and barium sulfate; two zinc sulfide pigments, zinc sulfide and a composite of zinc sulfide and barium sulfate; two calcium carbonates, one precipitated, and one water-ground. Fillers are not added to book paper to adulterate it but to improve the printing quality of the sheet. They fill the interstices of the fiber network of the paper thus producing a more even surface, lend softness, and improve the opacity and, generally, the color of the sheet. The number of types of important fillers on the market has increased considerably in the last few years, but little is known about their effect on the permanence of paper. The selection of fillers for the papermaking tests of this study was limited, however, to only the more important types, as a complete study of fillers, as such, was not planned at this time.

The sizing agent was that most generally employed, rosin soap. It was prepared from rosin and soda ash and was precipitated with papermaker's alum, aluminum sulfate.

The fibrous materials employed covered the range of those commonly used in the fine printing papers, and, like the fillers, were obtained from commercial manufacturers. They consisted of sulfite pulp and soda pulp of the ordinary book-paper grade; three "purified" wood pulps produced by special cooking and bleaching treatment to obtain high purity and strength; new rags, the grade known commercially as No. 1 white shirt cuttings; and two grades of old rags, No. 1 old whites and "twos and blues."

III. PAPERMAKING EQUIPMENT

The Bureau paper mill is equipped for experimental manufacture of practically all types of paper under conditions which in general simulate those of industrial mills. A complete description and photographs of the equipment may be found in previous publications [5].

IV. PAPERMAKING PROCESSES

1. PREPARATION OF RAG HALF STUFF

The procedure followed in the preparation of the rag "half stuff" (partially pulped rags that have been boiled, washed, drawn out of weave, and bleached) was essentially the same as the general practice in the commercial production of high-grade papers from rags. It was described in a previous publication [3] of the series.

The amount of bleaching powder, containing 35 percent of available chlorine, required to produce the desired degree of whiteness varied with the color of the rags. The amount used, based on the oven-dry weight of the rags, for No. 1 white shirt cuttings was 0.1 to 0.2 percent; for No. 1 old whites, 0.3 percent; and for twos and blues, 1.0 percent.

2. BEATER AND PAPER-MACHINE OPERATIONS

To afford comparison of the papers made in the numerous experimental runs it was necessary to follow a uniform procedure for handling the papermaking materials and the paper machine. It was desired that the procedure conform to customary or established general mill practice, but inasmuch as different mills differ widely as

to the relative time of adding the pulps, fillers, rosin, and alum to the beater, the method used was the one ordinarily followed at the Bureau and previously found to compare favorably with commercial mill methods.

The fillers were mixed with water (made into "slips") and the mixture agitated a fixed length of time and then run through an 80-mesh screen to remove dirt and impurities before being added to the beater.

The procedure followed in furnishing the beater, unless noted otherwise elsewhere in the text, was as follows: The pulps or fibrous materials and the filler slip were put in at the time of furnishing (which required about 15 minutes), and the rosin size was added to the stock 1 hour, and the alum ½ hour, before it was dropped to the beater chest. Variation from this procedure might have affected the characteristics of the finished sheet as to bulk, opacity, etc., but it is believed that it did not affect the permanence of the paper, which is the property of primary interest in this study.

The beating procedure was adjusted to the peculiarities of the different papermaking fibers. The paper-machine operations were the same for all runs. The methods of beating and paper-machine operation followed very closely those described in the other publications of this investigation [1, 2, 3].

The temperature of the stock at the head box of the paper machine was maintained at 90° F ±2°.

V. TESTING METHODS

All the physical and most of the chemical tests of the pulps and papers were made by the official methods[2] of the Technical Association of the Pulp and Paper Industry. For the determinations of the amounts of alpha-, beta-, and gamma-cellulose, pentosans, and acidity in the cellulosic materials, the methods used were modifications recently developed at the Bureau [6].[3] Although all papers were tested for acidity by the modified method (cold extraction), some of them were tested also by the TAPPI method (hot extraction), and for the latter the values obtained by both methods are reported. For the mill waters—in the beater and the head box—the pH determinations were made electrometrically, using the quinhydrone method except for the runs with calcium carbonate, for which a glass electrode was used because of the alkalinity.

The relative stability of papers can be judged by determining their chemical characteristics, but in addition it is desirable to subject them to some form of accelerated aging. Therefore, the pertinent physical and chemical tests were applied not only to the original papers but also to samples that had been submitted to an accelerated aging test considered to closely simulate the effects of natural aging. This test is made by heating specimens of the papers for 72 hours at 100° C and then conditioning and determining to what extent the paper has been altered in folding endurance, tearing strength, alpha-cellulose content, and copper number. For details of the accelerated aging test the reader is referred to previous discussions of the method [7].

[2] Copies of the methods can be obtained from the Technical Association of the Pulp and Paper Industry, 22 East 42d Street, New York, N. Y.

[3] Pentosans and acidity determined by unpublished methods.

VI. ANALYSES OF PAPERMAKING MATERIALS USED

1. FIBERS

Analyses showing the degree of cellulosic purity of the wood pulps and the rag half stuffs used in the manufacture of the papers are given in table 1. The fibrous material ranged in quality from 74 to 95 percent of alpha-cellulose and from 4.4 to 0.3 in copper number.

TABLE 1.—*Chemical test data on fibrous materials used*

Fibrous material	Alpha-cellulose [1]	Beta-cellulose [1]	Gamma cellulose [1]	Pentosans	Copper number	Ash [2]	Resin [3]
	%	%	%	%		%	%
Sulfite pulp	82.0	5.8	12.2	5.8	3.4	0.1	0.6
Soda pulp	74.4	21.3	4.3	18.7	4.4	.3	.2
Purified wood pulp *A* [3]	91.0	4.2	4.8	3.2	0.6	.1	.2
Purified wood pulp *C* [3]	88.3	6.3	5.4	4.3	.8	.1	.2
Purified wood pulp *D* [3]	84.2	4.3	11.5	8.4	.6	.2	.1
No. 1 new white rags, bleached half stuff	94.8	4.7	0.5	----	.3	.1	.2
No. 1 old white rags, bleached half stuff	90.3	9.4	.3	----	.4	.2	.2
Twos and blues, bleached half stuff	91.1	8.6	.3	----	.4	.3	.3

[1] Based on total cellulose.
[2] On oven-dry basis.
[3] Produced commercially by special cooking and bleaching treatment to obtain improved quality.

2. FILLERS

The chemical composition of the fillers used is shown in table 2.

TABLE 2.—*Composition of fillers used* [1]

Test	Clay	Titanium dioxide pigment *A*	Titanium dioxide pigment *B*	Zinc sulfide pigment *A*	Zinc sulfide pigment *B*	Precipitated calcium carbonate	Water-ground natural calcium carbonate
	%	%	%	%	%	%	%
Loss at 105° C	0.3	None	0.09	0.09	0.07	0.15	0.03
Further loss on ignition	13.7	0.15	None	16.1	9.0	43.6	43.8
Silica (SiO_2)	45.3	----	----	----	----	----	----
Iron oxide (Fe_2O_3)	0.2	----	----	----	----	----	----
Alumina (Al_2O_3)	38.8	----	----	----	----	----	----
Titanium dioxide (TiO_2)	1.8	98.2	30.4	----	----	----	----
Calcium carbonate ($CaCO_3$)	----	----	----	----	----	97.6	99.8
Barium sulfate ($BaSO_4$)	----	----	69.5	----	44.9	----	----
Zinc sulfide (ZnS)	----	----	----	99.8	54.8	----	----

[1] Analyses by Chemistry Division, National Bureau of Standards.

VII. DATA ON PAPERS MADE

1. PHYSICAL AND CHEMICAL MEASUREMENTS

Data relative to the composition of the beater furnishes (materials blended in the beater) and the various physical and chemical measurements on the papers made are given in tables 3 and 4.

The percentage of filler in paper is sometimes determined from the ash content, and sometimes, when possible, by chemical analysis. In the case of clay it was determined from the ash of the paper, corrected for the loss of water of composition from the clay during ignition. The values for the pigments were obtained by chemical analysis.

The amount of retention of filler is that proportion of the filler added to the beater furnish which appears in the finished paper. The different methods used in different laboratories for computing retention account in some degree for the varying results reported by them. The formula used in this work was developed by Edwin Sutermeister of the S. D. Warren Co., Cumberland Mills, Maine, and has been used in previous studies [8] carried on at the Bureau, in which it was found to check the determinations by weight. The formula is:

$$\text{Retention}=\frac{0.94(100-C-A)}{A(100-C-B)},$$

in which A is the percentage of ash in bone-dry stock going to machine (that is, the stuff box stock); B is the percentage of ash in bone-dry paper at reel; and C is the percentage of bone-dry filler lost on ignition.

Before being adopted for general use in a mill, however, this or any retention formula should be tested to determine whether it is suited to the particular conditions with which that mill has to deal. Many factors other than filler influence retention, but it is impossible to estimate their effects except in a general way. Some of the conditions which affect the retention of fillers are the kind of stock used, the extent of its beating (hydration), consistency of pulp and the amount of filler added, acidity, weight of paper made, speed of machine, chemicals used (such as starch, sodium silicate, or viscose materials), the use of save-alls, etc.

(a) CLAY-FILLED PAPERS

(1) *Sulfite pulp, 50 percent; soda pulp, 50 percent.*—Two paper-machine runs were made of sulfite and soda pulps without filler—one (run 1133), without rosin size or alum; the other (run 1143), with rosin size and alum added. The test data on the runs are given in tables 3 and 4. For the paper made from pulp alone (run 1133) the chemical test data for the heat-treated paper differ little from those for the original sheet, but when rosin and alum were added the alpha-cellulose content decreased and the copper number increased for the aged or heat-treated paper. The stability as regards retention of folding endurance and tearing strength is not high for either of the papers, with or without rosin size and alum.

TABLE 3.—*Papermaking details and physical test data on the book papers*

Paper machine run number	Beater furnish: Fiber	Beater furnish: Filler: Kind	Beater furnish: Filler: Amount [1]	Beater furnish: Rosin [1]	Beater furnish: Alum [2]	Acidity at headbox (quinhydrone method)	Tests of unheated papers [5]: Weight: 25 by 40 inches, 500 sheets	Bursting strength [3]	Tensile properties: Breaking load [4]: Machine direction	Tensile properties: Breaking load [4]: Cross direction	Tensile properties: Elongation at rupture: Machine direction	Tensile properties: Elongation at rupture: Cross direction	Thickness	Sizing value (dry-indicator method)	Opacity (contrast ratio)	Folding endurance [6]: Schopper: Machine direction	Folding endurance [6]: Schopper: Cross direction	Folding endurance [6]: MIT: Machine direction [7]	Folding endurance [6]: MIT: Cross direction [7]	Tearing strength: Machine direction	Tearing strength: Cross direction	Tests of heat-treated papers [8]: Folding endurance: Schopper	Tests of heat-treated papers [8]: Folding endurance: MIT	Tests of heat-treated papers [8]: Tearing strength
			%	%	%	pH	lb.	Points	kg	kg	%	%	in.	sec.	%	Double folds	Double folds	Double folds	Double folds	g	g	% of initial	% of initial	% of initial
1133	Sulfite pulp, 50%; soda pulp, 50%.	None	None	None	None	7.3	57.6	31	7.6	4.6	2.0	5.5	0.0035	----	81	247	141	2,828	1,228	55	54	39	69	80
1143	do	do	None	1	1.3	5.1	55.9	28	7.0	4.0	2.0	5.5	.0037	49	83	403	118	2,884	683	59	70	36	60	75
1134	do	Clay	15	None	0.5	7.0	55.8	26	6.0	3.6	2.0	5.0	.0035	----	86	101	38	1,749	395	47	51	57	72	89
1135	do	do	15	None	1.0	6.0	55.8	26	6.1	3.4	2.0	4.5	.0036	----	87	72	33	913	416	48	55	64	93	87
1130	do	do	15	None	1.5	4.6	55.5	24	5.5	3.7	1.8	5.0	.0035	----	87	53	33	548	423	48	49	46	56	80
1129	do	do	15	None	2.1	4.2	54.9	23	5.7	3.3	1.7	4.6	.0035	----	87	54	18	599	140	46	51	21	19	58
1136	do	do	15	2	1.1	5.8	56.8	25	5.8	3.3	2.0	5.0	.0037	41	87	71	25	857	355	49	57	58	78	80
1137	do	do	15	2	1.4	4.9	55.6	24	5.6	2.9	2.0	5.0	.0037	40	88	36	14	505	97	50	60	68	63	83
1138	do	do	15	2	2.3	4.2	57.3	18	3.8	2.9	2.0	4.5	.0037	59	90	41	14	443	111	53	57	49	53	73
1139	do	do	15	1	0.8	6.2	54.9	21	5.7	3.2	2.0	5.0	.0036	45	87	83	30	1,341	340	49	56	62	69	87
1140	do	do	15	1	1.3	5.1	56.1	20	5.3	3.0	2.0	4.5	.0036	42	88	47	23	731	142	51	52	59	70	84
1141	do	do	15	1	2.4	4.2	57.6	16	5.1	2.7	2.0	5.0	.0037	47	89	29	15	346	87	50	57	37	40	68
1142 [9]	do	do	15	1	[9] 2.4	[9] 6.1	55.7	18	4.6	2.7	2.5	5.0	.0036	48	89	27	13	329	96	46	53	77	76	90
1147	do	Titanium pigment *A*	15	1	1.3	4.8	54.9	16	4.9	2.6	1.5	5.0	.0035	38	94	29	14	317	82	49	54	61	77	82
1145	do	do	5	1	1.6	5.0	57.1	23	6.7	3.7	2.0	5.0	.0037	59	90	140	51	1,467	572	56	61	46	82	78
1148	do	Titanium pigment *B*	15	1	1.1	5.0	56.8	19	5.6	3.2	2.0	5.0	.0037	55	90	72	23	1,241	227	49	56	38	47	80
1149	do	do	15	1	2.2	4.2	56.5	16	5.2	2.7	2.0	5.0	.0035	45	92	39	15	540	132	47	54	32	32	72
1150	do	Zinc sulfide pigment *A*	15	1	1.2	4.9	56.0	19	5.2	2.9	2.0	5.5	.0035	44	91	52	22	832	172	54	58	63	69	77
1151	do	do	5	1	1.3	5.0	55.1	25	6.7	3.9	2.0	5.0	.0034	59	88	163	52	2,200	834	58	63	49	53	78
1152	do	Zinc sulfide pigment *B*	15	1	1.2	5.0	54.5	18	5.3	2.8	2.0	5.0	.0034	47	92	42	21	808	221	56	59	69	56	85
1153	do	do	15	1	2.3	4.2	55.0	14	4.6	2.5	1.5	4.5	.0033	47	94	20	10	250	64	50	58	52	60	72

See footnotes at end of table.

TABLE 3.—*Papermaking details and physical test data on the book papers*—Continued

Paper machine run number	Beater furnish: Fiber	Beater furnish: Filler: Kind	Beater furnish: Filler: Amount [1]	Beater furnish: Rosin [1]	Beater furnish: Alum [2]	Acidity at headbox (quinhydrone method)	Tests of unheated papers [3]: Weight: 25 by 40 inches, 500 sheets	Bursting strength [3]	Tensile properties: Breaking load [4]: Machine direction	Tensile properties: Breaking load [4]: Cross direction	Tensile properties: Elongation at rupture: Machine direction	Tensile properties: Elongation at rupture: Cross direction	Thickness	Sizing value (dry-indicator method)	Opacity (contrast ratio)	Folding endurance [5]: Schopper: Machine direction	Folding endurance [5]: Schopper: Cross direction	Folding endurance [5]: MIT: Machine direction [7]	Folding endurance [5]: MIT: Cross direction [7]	Tearing strength: Machine direction	Tearing strength: Cross direction	Tests of heat-treated papers [3]: Folding endurance: Schopper	Folding endurance: MIT	Tearing strength
			%	%	%	*pH*	*lb*	*Points*	*kg*	*kg*	%	%	*in.*	*sec*	%	*Double folds*	*Double folds*	*Double folds*	*Double folds*	*g*	*g*	% of initial	% of initial	% of initial
1158	Sulfite pulp, 50%; soda pulp, 50%.	Prec. calcium carbonate.	15	None	None	[10] 8.2	56.0	20	5.3	3.1	3.0	5.0	.0037	0	90	57	23	644	150	51	55	67	77	92
1159	do	do	15	2	1.1	[10] 8.0	56.6	16	4.8	2.6	2.5	5.0	.0038	21	92	33	12	201	70	51	59	76	98	90
1172	do	do	15	2	1.1	[10] 8.0	56.9	19	4.2	2.6	1.5	3.0	.0039	13	92	21	17	251	122	50	52	74	55	91
1173	do	do	30	2	1.0	[10] 8.0	55.9	15	3.1	1.9	1.0	3.0	.0037	6	93	8	5	47	28	44	45	84	90	97
1174	do	Natural calcium carbonate *A*.	30	None	None	[10] 7.7	56.7	22	4.7	3.0	1.5	4.5	.0037	0	86	26	20	462	250	42	41	73	57	91
1175	do	do	15	2	1.0	[10] 7.7	56.4	23	5.0	3.3	1.0	4.5	.0037	23	87	38	21	445	135	45	47	66	75	93
1220	do	Natural calcium carbonate *C*.	30	2	1.0	[10] 7.8	55.4	14	3.3	2.0	2.0	4.0	.0034	11	93	10	6	59	28	42	45	82	78	92
1160	Purified wood pulp: *A*, 75%; *C*, 25%.	Clay	15	None	None	7.0	58.0	25	5.8	3.2	3.5	7.0	.0037	0	87	840	118	5,310	1,890	83	95	90	110	99
1161	do	do	15	2	0.8	5.9	55.0	21	5.0	2.5	2.5	5.5	.0034	24	88	260	43	2,270	474	82	96	106	108	90
1162	do	do	15	2	1.1	4.8	57.4	21	4.8	2.6	2.0	5.5	.0036	31	87	211	37	1,734	428	79	84	92	97	90
1163	do	do	15	2	2.3	4.2	57.0	22	5.3	2.7	2.5	6.0	.0036	35	87	325	47	2,328	556	77	87	69	81	80
1164	do	do	15	1	0.6	5.6	56.5	23	5.2	2.6	2.5	6.0	.0033	13	87	274	41	3,506	487	79	86	109	93	91
1165	do	do	15	1	0.8	4.7	58.1	23	5.1	2.6	3.0	5.5	.0036	22	88	242	47	2,480	592	83	91	84	95	80
1166	do	do	15	1	2.1	4.2	56.0	23	5.3	2.5	3.0	6.0	.0037	24	88	221	45	2,646	696	75	85	69	62	74
1167	Purified wood pulp: *D*, 100%.	do	15	None	None	7.0	55.8	37	9.0	4.7	4.5	9.0	.0034	4	80	2,800	2,313	[11] 1,763	[11] 1,761	97	101	101	86	102
1168	do	do	15	1	0.7	6.1	55.1	37	8.3	4.4	4.0	9.0	.0033	14	83	2,633	2,077	[11] 1,490	[11] 1,441	99	101	89	84	99
1169	do	do	15	1	1.0	4.9	56.9	36	8.0	4.8	4.0	10.0	.0036	17	84	1,952	1,920	[11] 1,118	[11] 1,297	112	126	91	77	81
1170	do	do	15	1	2.3	4.2	56.6	36	8.0	4.4	4.0	8.0	.0034	22	84	2,067	1,688	[11] 1,096	[11] 752	108	108	46	47	66
1176	Rags: No. 1 new whites, 100%.	do	15	None	0.5	6.6	56.4	21	4.4	2.8	2.5	5.0	.0036	0	88	140	40	1,675	642	94	110	108	92	100

1176	Rags: No. 1 new whites, 100%.	do	15	None	0.5	6.6	56.4	21	4.4	2.8	2.5	5.0	.0036	0	88	140	40	1,675	642	94	110	108	92	100
1177	do	do	15	None	0.8	4.9	55.9	21	4.4	2.7	2.0	5.0	.0035	0	88	103	29	1,059	416	84	94	102	118	101
1178	do	do	15	None	1.5	4.2	55.0	20	4.4	2.6	2.0	5.0	.0035	0	88	100	29	1,541	474	89	95	101	101	88
1179	do	do	15	2	0.9	6.6	55.7	20	4.4	2.7	2.0	4.5	.0034	2	88	83	32	1,062	351	85	90	100	113	98
1180	do	do	15	2	1.2	4.9	56.1	20	4.4	2.5	2.0	5.0	.0034	9	89	71	20	543	220	85	90	129	109	94
1181	do	do	15	2	2.0	4.2	54.9	16	4.1	2.6	2.0	5.0	.0033	7	89	55	25	460	253	80	85	96	99	87
1182	do	do	15	2	4.0	4.0	54.8	17	4.2	2.7	2.0	5.0	.0033	11	88	63	28	651	291	82	81	96	86	89
1183	do	do	15	1	0.7	6.5	55.5	19	4.3	2.8	2.0	5.5	.0033	2	87	90	36	1,482	403	88	85	106	92	95
1184	do	do	15	1	1.1	4.8	55.0	18	4.2	2.7	2.0	5.5	.0035	3	88	76	28	810	246	81	90	99	108	96
1185	do	do	15	1	2.0	4.2	56.0	17	4.1	2.8	2.0	5.5	.0035	5	88	68	36	735	357	87	92	101	93	87
1186	do	do	15	1	4.0	4.0	54.3	19	4.5	2.9	2.0	6.0	.0034	5	86	79	37	1,090	517	86	85	77	69	80
1191	**Rags: No. 1 old whites, 50%; two and blues, 50%.**	do	15	None	0.7	6.7	56.4	15	3.3	2.2	2.5	4.0	.0036	0	91	13	8	71	55	55	60	107	114	97
1192	do	do	15	None	1.3	4.9	57.1	14	3.2	2.2	2.0	4.0	.0038	1	91	11	7	66	48	57	61	100	114	92
1193	do	do	15	None	2.1	4.2	56.0	15	3.4	2.2	2.5	4.5	.0036	1	92	13	7	76	53	56	59	78	95	90
1200	do	do	15	2	1.0	6.5	57.2	16	3.6	2.2	2.5	4.0	.0037	3	91	14	7	80	61	58	63	107	130	93
1201	do	do	15	2	1.5	4.8	56.5	14	3.1	2.2	2.5	4.5	.0035	6	92	10	6	56	38	54	58	105	98	93
1202	do	do	15	2	2.1	4.2	54.8	14	3.2	2.1	2.5	4.5	.0037	5	91	11	6	51	33	52	56	87	100	92
1203	do	do	15	2	4.0	4.0	56.1	14	3.0	2.2	2.5	4.5	.0037	6	91	11	7	64	37	54	57	84	100	91
1214	do	None	None	1	1.1	5.0	55.1	22	4.1	3.0	2.5	5.0	.0038	3	86	49	22	524	267	62	67	96	138	93
1204	do	Clay	15	1	1.0	6.3	56.9	17	3.2	2.3	2.5	4.5	.0039	3	91	13	8	87	61	56	55	92	86	95
1205	do	do	15	1	1.3	4.9	55.9	15	3.1	2.2	2.5	4.5	.0038	3	91	13	6	66	42	53	57	89	109	91
1206	do	do	15	1	2.2	4.2	56.9	16	2.9	2.3	2.5	4.5	.0039	4	91	12	7	72	47	55	57	87	102	86
1207	do	Titanium pigment A	5	1	1.4	4.9	57.4	19	3.7	2.7	2.5	5.0	.0038	6	92	24	12	217	113	60	64	96	96	91
1208	do	Titanium pigment B	15	1	1.3	4.9	56.0	15	3.1	2.2	2.5	5.0	.0035	4	93	12	7	94	47	54	56	104	107	94
1209	do	do	15	1	2.2	4.2	57.1	15	3.1	2.3	2.5	5.0	.0037	5	93	14	7	97	53	55	57	103	97	93
1210	do	Zinc sulfide pigment A	5	1	1.6	4.9	56.4	17	3.3	2.5	2.5	5.0	.0039	5	94	19	10	130	88	60	64	95	108	90
1211	do	Zinc sulfide pigment B	15	1	1.5	4.9	57.5	15	3.0	2.1	2.5	4.5	.0037	3	95	12	6	78	47	56	58	108	112	91
1212	do	do	15	1	2.3	4.2	57.4	14	3.0	2.1	2.5	4.5	.0037	3	95	12	6	62	39	57	56	96	114	85
1215	do	Prec. calcium carbonate	15	None	None	[10] 8.1	55.2	15	3.3	2.2	3.0	4.5	.0036	----	91	19	9	102	65	54	57	100	125	98
1216	do	do	30	None	None	[10] 8.4	55.3	11	2.2	1.7	2.0	4.0	.0033	----	93	6	4	28	25	45	49	92	92	97
1217	do	Natural calcium carbonate C.	15	None	None	[10] 8.1	56.4	17	3.7	2.5	2.5	4.5	.0037	----	90	16	10	191	95	58	62	120	85	95
1218	do	Natural calcium carbonate B.	15	None	None	[10] 8.1	55.6	17	3.6	2.5	3.0	4.5	.0037	----	89	23	13	200	136	57	54	102	96	99
1219	do	Natural calcium carbonate A.	15	None	None	[10] 8.0	55.9	18	3.5	2.5	2.5	5.0	.0037	----	89	23	11	277	106	53	59	113	88	98

[1] Based on dry weight of fiber and filler.
[2] Based on dry weight of fiber, filler, and rosin.
[3] Bursting pressure, in pounds per square inch, through a circular orifice 1.2 inches in diameter.
[4] For test specimen 15 mm wide and 100 mm between jaws.
[5] All physical tests made at 65-percent relative humidity and 70° F.
[6] Test specimen 15 mm wide.
[7] Tests made at 0.5-kg tension unless noted.
[8] Samples heated at 100° C for 72 hours.
[9] See text, p. 683. An excessive amount of alum was added in the beater to give pH 4.2, but later sodium carbonate was added to neutralize part of the acidity.
[10] Glass-electrode method.
[11] Tests made at 1.0-kg tension.

TABLE 4.—*Papermaking details and chemical test data on the book papers*

Paper machine run number	Beater furnish: Fiber	Beater furnish: Filler: Kind	Beater furnish: Filler: Amount [1]	Beater furnish: Rosin [1]	Beater furnish: Alum [2]	Acidity at head box (quinhydrone method)	Original papers: Ash [3]	Original papers: Filler	Original papers: Retention of filler [4]	Original papers: Resin [2]	Original papers: Acidity (glass-electrode method): Cold-water extraction	Original papers: Acidity (glass-electrode method): Hot-water extraction	Original papers: Alpha-cellulose [5]	Original papers: Beta-cellulose [5]	Original papers: Gamma-cellulose [5]	Original papers: Pentosans	Original papers: Copper number	Heat-treated papers [6] (change in content): Alpha-cellulose	Heat-treated papers [6] (change in content): Beta-cellulose	Heat-treated papers [6] (change in content): Gamma-cellulose	Heat-treated papers [6] (change in content): Pentosans	Heat-treated papers [6] (change in content): Copper number
			%	%	%	pH	%	%		%	pH	pH	%	%	%	%		%	%	%	%	
1133	Sulfite pulp, 50%; soda pulp, 50%.	None	None	None	None	7.3	0.3			0.3	6.9	6.4	75.8	17.3	6.9	11.2	3.2	+0.1	−0.5	+0.4	0	−0.1
1143	do	do	None	1	1.3	5.1	.4			.9	5.8	5.1	75.4	17.2	7.4	10.7	3.3	−2.0	+1.7	+.3	+0.3	+.3
1134	do	Clay	15	None	0.5	7.0	7.8	8.6	0.56	.3	6.6	6.2	74.8	18.0	7.2	11.1	3.0	−1.0	+0.2	+.8	−.1	−.1
1135	do	do	15	None	1.0	6.0	8.0	8.9	.60	.3	6.4	5.7	74.4	17.6	8.0	10.2	3.2	−1.2	+.7	+.5	+.2	.0
1130	do	do	15	None	1.5	4.6	9.1	10.1	.66	.2	5.3	4.8	75.7	16.8	7.5	11.4	3.6	−3.3	+2.8	+.5	+.9	+.4
1129	do	do	15	None	2.1	4.2	10.1	11.2	.77	.2	4.9	4.3	76.0	16.3	7.7	11.4	3.6	−7.6	+7.2	+.4	+.6	+.6
1136	do	do	15	2	1.1	5.8	7.8	8.5	.52	1.2	6.0	5.3	77.0	14.7	8.3	10.3	3.5	−4.0	+2.9	+1.1	+.5	+.7
1137	do	do	15	2	1.4	4.9	9.7	10.6	.67	1.6	5.5	4.9	76.8	15.0	8.2	10.6	3.6	−5.0	+4.6	+0.4	+.2	+.7
1138	do	do	15	2	2.3	4.2	10.2	11.2	.71	1.9	5.4	4.5	77.6	13.9	8.5	10.8	3.5	−5.8	+4.9	+.9	+.4	+.7
1139	do	do	15	1	0.8	6.2	8.1	8.8	.53	0.9	6.2	5.5	77.8	14.5	7.7	10.5	3.1	−2.6	+2.3	+.3	+.4	+.5
1140	do	do	15	1	1.3	5.1	9.2	10.0	.64	1.0	5.9	5.1	76.4	16.5	7.1	10.5	3.3	−3.2	+2.5	+.7	−.1	+.4
1141	do	do	15	1	2.4	4.2	10.8	11.8	.73	1.2	5.2	4.6	74.3	18.1	7.6	9.7	3.2	−6.3	+6.8	−.5	+1.2	+.7
1142 [7]	do	do	15	1	[7] 2.4	[7] 6.1	11.4	12.6	.80	1.0	6.5	5.3	75.0	17.6	7.4	10.7	3.2	−2.6	+2.5	+.1	+0.1	+.7
1147	do	Titanium pigment A.	15	1	1.3	4.8	9.7	9.0	.59	1.0	5.2	----	73.6	18.2	8.2	11.0	3.3	−5.0	+4.8	+.2	+.4	+.6
1145	do	do	5	1	1.6	5.0	3.8	3.1	.68	0.9	5.6	4.9	75.2	15.8	9.0	----	3.0	−5.2	+5.8	−.6	----	+.8
1148	do	Titanium pigment B.	15	1	1.1	5.0	7.4	[8] 2.1; 4.6	.44	.9	5.4	4.6	73.5	19.3	7.2	10.6	3.0	−6.0	+5.6	+.4	.0	+.3
1149	do	do	15	1	2.2	4.2	10.5	[8] 3.2; 6.6	.64	1.1	5.2	4.6	72.2	20.6	7.2	10.6	3.0	−8.2	+7.3	+.9	.0	+1.1
1150	do	Zinc sulfide pigment A.	15	1	1.2	4.9	8.5	9.4	.60	1.1	5.8	----	78.2	13.6	8.2	10.4	[10]	−3.7	+2.9	+.8	.0	[10]
1151	do	do	5	1	1.3	5.0	2.5	2.3	.52	0.9	5.7	----	76.8	15.0	8.2	9.6	[10]	−2.0	+1.2	+.8	−.7	[10]
1152	do	Zinc sulfide pigment B.	15	1	1.2	5.0	8.6	[9] 5.0; 4.0	.55	1.1	5.8	5.1	77.4	15.7	6.9	10.3	[10]	−3.7	+3.5	+.2	+.6	[10]
1153	do	do	15	1	2.3	4.2	11.2	[9] 6.2; 5.1	.74	1.2	5.1	4.6	77.3	13.9	8.8	10.7	[10]	−1.3	+0.1	+1.2	+.1	[10]
1158	do	Prec. calcium carbonate.	15	None	None	[11] 8.2	4.2	7.2	[12] .48	0.5	9.6	----	75.5	15.3	9.2	10.5	3.3	−0.4	+3.0	−2.6	0.0	+.9

1158	do	Prec. calcium carbonate.	15	None	None	[11] 8.2	4.2	7.2	[12] .48	0.5	9.6	----	75.5	15.3	9.2	10.5	3.3	−0.4	+3.0	−2.6	0.0	+0.
1159	do	do	15	2	1.1	[11] 8.0	6.3	11.2	[12] .75	1.5	9.2	----	76.6	15.7	7.7	10.1	3.3	−1.5	+1.0	+0.5	−1.3	+.1
1172	do	do	15	2	1.1	[11] 8.0	6.5	11.2	[12] .75	1.6	8.9	----	75.6	15.2	9.2	10.8	3.4	−2.1	+1.5	+.6	+0.5	+.4
1173	do	do	30	2	1.0	[11] 8.0	12.1	21.1	[12] .70	1.6	8.8	----	76.4	14.6	9.0	10.7	3.4	−2.3	+2.0	+.3	+.2	+.4
1174	do	Natural calcium carbonate *A*.	30	None	None	[11] 7.7	10.0	16.4	[12] .55	0.3	9.2	----	74.2	18.3	7.5	9.7	3.3	−2.2	+1.8	+.4	+.9	+.3
1175	do	do	15	2	1.0	[11] 7.7	6.0	9.9	[12] .66	1.3	8.5	----	74.2	17.4	8.4	10.7	3.3	−3.3	+2.9	+.4	+.1	+.3
1220	do	Natural calcium carbonate *C*.	30	2	1.0	[11] 7.8	12.6	21.2	[12] .70	1.1	8.8	----	75.0	17.5	7.5	------	3.8	−2.7	+1.7	+1.0	------	+.5
1160	Purified wood pulp: *A*, 75%; *C*, 25%.	Clay	15	None	None	7.0	7.6	8.4	.53	0.2	6.9	7.2	89.8	4.6	5.6	------	0.7	−0.4	−0.1	+0.5	------	+.1
1161	do	do	15	2	0.8	5.9	10.5	11.5	.76	1.6	6.1	5.7	90.2	4.0	5.8	------	.8	−.8	−.2	+1.0	------	+.3
1162	do	do	15	2	1.1	4.8	10.7	11.9	.79	1.7	5.6	5.3	90.2	2.8	7.0	------	.9	−3.6	+3.5	+0.1	------	+.5
1163	do	do	15	2	2.3	4.2	10.0	11.1	.74	1.9	5.2	4.5	90.0	3.4	6.6	------	.9	−4.6	+4.2	+.4	------	+.7
1164	do	do	15	1	0.6	5.6	10.9	12.1	.81	1.1	6.0	5.7	89.8	4.8	5.4	------	.9	−1.8	+1.5	+.3	------	+.2
1165	do	do	15	1	.8	4.7	10.7	11.9	.79	1.1	5.6	5.0	89.9	4.9	5.2	------	.8	−2.9	+2.5	+.4	------	+.4
1166	do	do	15	1	2.1	4.2	10.1	11.2	.74	1.0	5.0	4.4	89.6	4.7	5.7	------	.9	−5.0	+5.1	−.1	------	+.5
1167	Purified wood pulp: *D*, 100%.	do	15	None	None	7.0	9.8	10.8	.71	0.1	6.8	7.0	82.4	4.2	13.4	8.5	.7	−0.2	+0.2	.0	+.3	+.1
1168	do	do	15	1	0.7	6.1	12.1	13.5	.88	.9	6.4	6.0	83.2	4.4	12.4	8.5	.8	−.7	+.5	+.2	+.1	+.2
1169	do	do	15	1	1.0	4.9	12.5	13.9	.87	.9	5.8	5.0	82.6	4.4	13.0	8.4	.7	−.8	+.8	.0	+.1	+.1
1170	do	do	15	1	2.3	4.2	12.3	13.7	.84	1.0	5.2	4.4	82.4	4.6	13.0	8.3	1.1	−1.4	+2.9	−1.5	+.2	+.3
1176	Rags: No. 1 new whites, 100%.	do	15	None	0.5	6.6	11.4	12.6	.81	0.3	7.2	7.3	96.0	3.2	0.8	------	0.2	−.03	+0.3	0.0	------	+.1
1177	do	do	15	None	.8	4.9	12.6	14.0	.89	.3	6.4	5.5	95.8	3.4	.8	------	.2	−0.9	+.7	+.2	------	+.2
1178	do	do	15	None	1.5	4.2	11.6	12.7	.82	.2	5.5	4.8	95.2	4.1	.7	------	.3	−3.2	+3.0	+.2	------	+.2
1179	do	do	15	2	0.9	6.6	11.2	12.4	.80	1.6	6.4	5.9	96.0	2.6	1.4	------	.4	−2.0	+1.6	+.4	------	+.4
1180	do	do	15	2	1.2	4.9	12.3	13.6	.87	1.8	5.6	5.0	94.8	3.7	1.5	------	.5	−4.6	+4.1	+.5	------	+.5
1181	do	do	15	2	2.0	4.2	11.8	13.0	.83	1.7	5.4	4.7	95.1	3.6	1.3	------	.4	−5.3	+4.7	+.6	------	+.6
1182	do	do	15	2	4.0	4.0	11.8	13.0	.83	1.7	5.0	4.4	94.8	4.0	1.2	------	.5	−7.0	+6.2	+.8	------	+.7
1183	do	do	15	1	0.7	6.5	11.6	12.7	.82	0.8	6.3	6.0	95.8	3.4	0.8	------	.3	−1.4	+1.1	+.3	------	+.2
1184	do	do	15	1	1.1	4.8	12.3	13.6	.87	.9	5.6	5.0	95.4	3.6	1.0	------	.3	−2.9	+2.7	+.2	------	+.4
1185	do	do	15	1	2.0	4.2	11.6	12.7	.84	.9	5.1	4.5	95.1	4.1	0.8	------	.4	−4.9	+4.6	+.3	------	+.4
1186	do	do	15	1	4.0	4.0	10.8	12.0	.82	.9	4.9	4.3	95.0	4.2	.8	------	.4	−8.0	+7.6	+.4	------	+.5
1191	Rags: No. 1 old whites, 50%; twos and blues, 50%.	do	15	None	0.7	6.7	12.5	13.9	.84	.2	6.8	----	92.3	7.5	.2	------	.3	−3.1	+1.4	+1.7	------	+.1
1192	do	do	15	None	1.3	4.9	12.4	13.8	.83	.2	5.8	----	91.1	8.7	.2	------	.4	−3.0	+1.8	+1.2	------	+.1
1193	do	do	15	None	2.1	4.2	12.4	13.8	.83	.3	5.1	----	91.6	8.3	.1	------	.5	−8.1	+7.3	+0.8	------	+.2
1200	do	do	15	2	1.0	6.5	11.7	13.0	.79	1.4	6.7	----	90.4	8.2	1.4	------	.5	−4.0	+3.6	+.4	------	+.5
1201	do	do	15	2	1.5	4.8	12.3	13.7	.85	1.4	5.9	5.1	89.0	9.5	1.5	------	.5	−6.6	+5.9	+.7	------	+.9
1202	do	do	15	2	2.1	4.2	12.3	13.7	.84	1.5	5.5	4.8	89.1	9.3	1.6	------	.7	−8.3	+7.6	+.7	------	+.8
1203	do	do	15	2	4.0	4.0	12.1	13.4	.83	1.5	5.3	4.5	89.2	9.3	1.5	------	.7	−9.6	+8.8	+.8	------	+.9

See footnotes at end of table.

TABLE 4.—*Papermaking details and chemical test data on the book papers*—Continued

Paper machine run number	Beater furnish					Acidity at head box (quinhydrone method)	Original papers												Heat-treated papers [6] (change in content)				
	Fiber	Filler		Rosin [1]	Alum [2]		Ash [3]	Filler	Retention of filler [4]	Resin	Acidity (glass-electrode method)		Alpha-cellulose [5]	Beta-cellulose [5]	Gamma-cellulose [5]	Pentosans	Copper number	Alpha-cellulose	Beta-cellulose	Gamma-cellulose	Pentosans	Copper number
		Kind	Amount [1]								Cold-water extraction	Hot-water extraction										
			%	%	%	pH	%	%		%	pH	pH	%	%	%	%		%	%	%	%	
1214	Rags: No. 1 whites, 50%; twos and blues, 50%.	None	None	1	1.1	5.0	0.4			0.5	6.2		90.3	8.6	1.1		.4	−3.0	+2.8	+.2		+.3
1204	do	Clay	15	1	1.0	6.3	12.1	13.4	.82	.5	6.2		90.4	8.6	1.0		.4	−2.9	+2.8	+.1		+.3
1205	do	do	15	1	1.3	4.9	12.6	14.0	.87	.5	5.4		89.6	9.5	0.9		.6	−4.2	+3.6	+.6		+.4
1206	do	do	15	1	2.2	4.2	12.2	13.5	.84	.7	5.0		90.0	9.1	.1		.6	−6.7	+6.4	+.3		+.4
1207	do	Titanium pigment *A*.	5	1	1.4	4.9	5.0	4.6	.87	.8	5.2		90.2	8.8	1.0		.5	−4.4	+3.9	+.5		+.5
1208	do	Titanium pigment *B*.	15	1	1.3	4.9	13.4	[8]4.2; 8.1	.82	.9	5.7		90.5	9.5	0.0		.4	−3.7	+3.6	+.1		+.4
1209	do	do	15	1	2.2	4.2	13.7	[8]4.2; 8.4	.83	.8	5.6		89.8	10.1	.1		.6	−4.3	+4.4	−.1		+.4
1210	do	Zinc sulfide pigment *A*.	5	1	1.6	4.9	4.2	4.3	.85	.8	6.1		90.5	9.0	.5		(10)	−5.1	+4.4	+.7		(10)
1211	do	Zinc sulfide pigment *B*.	15	1	1.5	4.9	12.8	[9]7.2; 5.8	.85	.9	6.2		91.0	8.1	.9		(10)	−4.7	+4.3	+.4		(10)
1212	do	do	15	1	2.3	4.2	12.4	[9]6.9; 5.6	.83	.9	5.5		90.7	8.8	.5		(10)	−6.8	+6.1	+.7		(10)
1215½	do	Prec. calcium carbonate.	15	None	None	[11]8.1	8.3	14.0	[12].93	.1	9.5		92.8	6.7	.5		.4	−0.6	+0.3	+.3		.0
1216	do	do	30	None	None	[11]8.4	16.5	28.2	[13].94	.1	9.5		92.7	6.6	.7		.3	+.1	−.3	+.2		+.1
1217	do	Natural calcium carbonate *C*.	15	None	None	[11]8.1	6.9	11.8	[13].79	.1	9.4		92.5	6.9	.6		.3	−2.1	+2.1	.0		+.1
1218	do	Natural calcium carbonate *B*.	15	None	None	[11]8.1	7.3	12.4	[13].82	.2	9.4		92.4	7.0	.6		.4	−2.7	+2.5	+.2		+.1
1219	do	Natural calcium carbonate *A*.	15	None	None	[11]8.0	7.3	12.2	[13].81	.2	9.4		92.1	7.3	.6		.4	−1.4	+1.5	−.1		+.1

[1] Based on dry weight of fiber and filler.
[2] Based on dry weight of fiber, filler, and rosin.
[3] On oven-dry basis.
[4] For method of calculating retention see text, p. 676.
[5] Based on total cellulose.
[6] Samples heated at 100° C for 72 hours.
[7] See text, p. 683. An excessive amount of alum was added in the beater to give pH 4.2, but later sodium carbonate was added to neutralize part of the acidity.
[8] Titanium dioxide and barium sulfate, respectively.
[9] Zinc sulfide and barium sulfate, respectively.
[10] Presence of zinc sulfide interferes with the chemical reactions in the test.
[11] Glass-electrode method.
[12] Approximated, did not have data required for use of formula. Obtained by dividing percentage in paper by percentage furnished.

A series of runs (1134, 1135, 1130, and 1129) of unsized papers containing clay was made in which the amount of alum added was varied. The effect of acidity on the stability of the unsized clay-filled papers is shown by the decrease in alpha-cellulose content and increase in copper number of the heat-treated papers as the amount of alum in the furnish increased, and the decrease in retention of folding endurance and tearing strength. In general, the agreement between the pH values of the water from the stock at the head box and of the hot-water extraction of the finished paper was fairly good, the differences probably being due to differences in buffer conditions, the head-box sample being well buffered and the water extraction of the finished paper poorly buffered. The clay retention of the runs increased with increased amounts of alum.

To study the effect of rosin sizing on the stability of sulfite-soda papers containing clay several machine runs were made in which the amounts of alum and rosin size were varied.

The test data on the runs (1136 to 1138) in which the amount of rosin was kept constant at 2 percent and the amount of alum was varied show that the change in alpha-cellulose content of the heat-treated papers increased as the alum was increased, but that the increase in copper number remained constant, although large. The percentage of retention of folding endurance and tearing strength gradually decreased as acidity increased but to less extent than for the unsized papers, to which rosin was not added (runs 1134, 1135, 1130, and 1129). The rosin seems to have hindered deterioration. This phenomenon was noted also in a previous study [2] of sulfite pulps for writing papers. As a possible reason for this apparent disagreement, it is suggested that for pulps in the low stability range, rosin sizing may actually have a protective effect. The indications are that, within the range studied, the amount of rosin employed in sizing sulfite-soda papers is not an important consideration as far as stability is concerned. Retention of clay in runs 1136 to 1138 increased as alum was increased.

For the series of papers (runs 1139 to 1141) in which the amount of rosin was kept constant at 1 percent and the amount of alum was varied, the stability falls between that of papers with no rosin in the beater furnish and those with 2 percent of rosin added. The data on the heat-treated papers of this series are shown graphically in figure 1.

Although the folding strength of the original clay-filled papers decreased as the amount of alum was increased, some of the decrease was due to the increased retention of clay. The increased filler content should not affect the strength retention of the heat-treated papers, however, since clay is an inert substance which has been previously found to have no harmful effect on the stability of paper.

To determine whether paper made from stock having high acidity in the beater but subsequently adjusted at the paper machine to low acidity would remain stable, a paper-machine run (1142) was made similar to run 1141 in the preparation of the stock in the beater. An excessive amount of alum was added in the beater to give a pH of 4.2, but a solution of soda ash (sodium carbonate) was added to neutralize some of the acidity as the stock was being pumped from the beater chest to the machine chest. The pH at the head box of

the paper machine was 6.1. The stability of the finished paper compared favorably with that of the run (1139) which had pH 6.2 at the head box without any treatment to reduce the original acidity. The retention of folding endurance and tearing strength was as good for the paper of the adjusted run as for the run in which only a small amount of alum was used (run 1139), and the change in alpha-cellulose content of the heat-treated paper was no greater. But the increase in copper number was the same as that of the paper with high acidity at the head box (run 1141). The sizing value was not materially affected, but the clay retention was increased. The improvement in clay retention may be attributable to the presence of

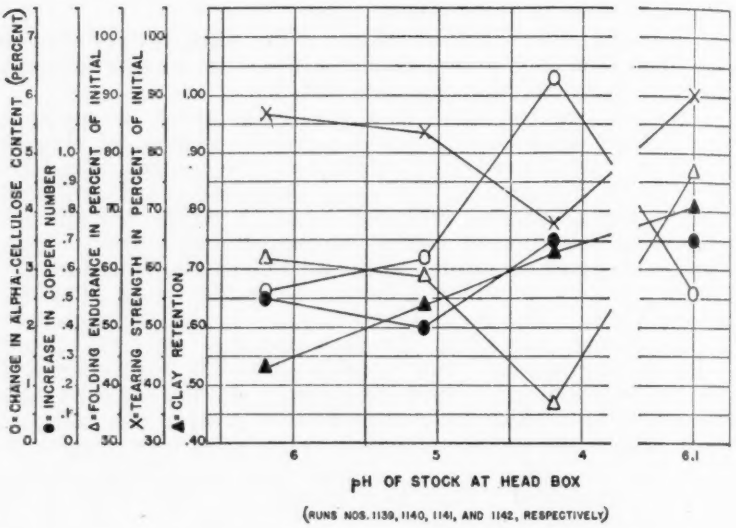

O=CHANGE IN ALPHA-CELLULOSE CONTENT (PERCENT)
●=INCREASE IN COPPER NUMBER
Δ=FOLDING ENDURANCE IN PERCENT OF INITIAL
X=TEARING STRENGTH IN PERCENT OF INITIAL
▲=CLAY RETENTION
pH OF STOCK AT HEAD BOX
(RUNS NOS. 1139, 1140, 1141, AND 1142, RESPECTIVELY)

FIGURE 1.—*Effect of acidity on stability of rosin-sized, clay-filled book papers made from sulfite and soda pulps.*

Points at pH 6.1 are displaced to right of main graph to avoid confusion. For this run there was considerable difference between the initial and final pH values. An excessive amount of alum was used in the beater to give a pH of 4.2, but sodium carbonate was added to neutralize part of the acidity as the stock was being pumped from the beater chest to the machine chest.

aluminum floc formed when the acidity caused by the excessive amount of alum was neutralized with the soda ash. Retention has been shown by a number of writers to be partly the result of occlusion and fixation of the finer particles in the sheet by the rosin and the aluminum hydrate floc formed in the sizing operation.

In addition to the results obtained on the experimental paper, tests at the Bureau on commercial papers of known history show that with high acidity in the beater followed by treatment at the paper machine to obtain low acidity, paper of fair stability, as far as acidity is concerned, may be produced.

The pentosan content of the different sulfite-soda papers was not appreciably changed by the heat treatment. It is apparent that pentosans do not contribute to the deterioration of cellulose to the extent that modified celluloses do, and therefore that pentosan

determinations are comparatively unimportant in evaluating the relative stability of papers.

(2) *Purified wood pulp: A, 75 percent; C, 25 percent.*—In previous work [4] at the Bureau on purified wood pulps, papers made from pulp *A* without rosin and alum were relatively stable but had comparatively low folding strength. Pulp *B* produced a hard sheet, stronger but less stable to the heat test, and not as good in color as that made from pulp *A*. The use of a small amount (25 percent of furnish) of pulp *B* with the weaker but more stable pulp *A* increased the strength of the sheet without appreciably lessening its stability. Paper made from pulp *C* showed that although pulp *C* was not so strong as pulp *B*, it was considerably stronger than *A* and produced a softer paper of better color

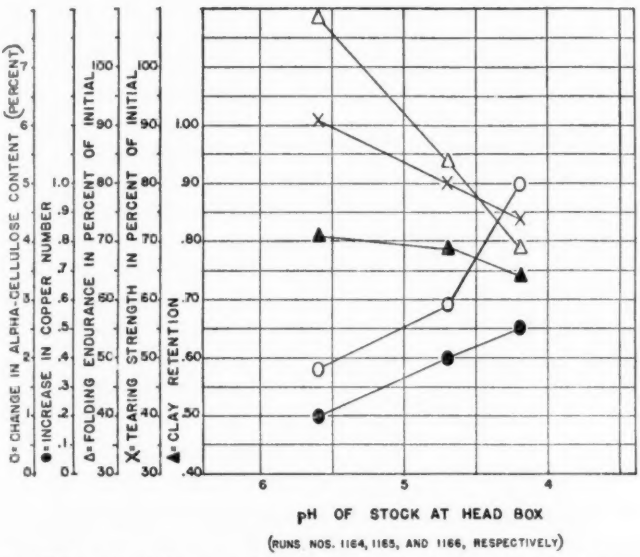

O= CHANGE IN ALPHA-CELLULOSE CONTENT (PERCENT)
●= INCREASE IN COPPER NUMBER
Δ= FOLDING ENDURANCE IN PERCENT OF INITIAL
X= TEARING STRENGTH IN PERCENT OF INITIAL
▲= CLAY RETENTION
pH OF STOCK AT HEAD BOX
(RUNS NOS. 1164, 1165, AND 1166, RESPECTIVELY)

FIGURE 2.—*Effect of acidity on stability of rosin-sized, clay-filled book papers made from purified wood pulps A and C.*

and stability than *B*. Therefore, pulp *C*, rather than *B*, was selected for mixture with purified wood pulp *A* in the present study to obtain improved strength.

One run (1160) was made of the mixture of pulps *A* and *C* with clay filler but without rosin size or alum to obtain data on the quality of the pulp mixture. To determine the effects of rosin size and alum on the stability of papers from the mixture, two series of runs were made—one (runs 1161 to 1163), with 2 percent of rosin size and various amounts of alum; the other (runs 1164 to 1166), with 1 percent of rosin and various amounts of alum. The data on the papers are given in tables 3 and 4. The stability of the second series (furnish containing 1 percent of rosin) is also shown graphically in figure 2.

The stability of the papers to the heat treatment decreased as the amount of alum was increased, and was little affected by rosin size. The clay retention was highest when the pH at the head box was 5.0 to 6.0 and lowest at the highest acidity, pH 4.2. The papers were of

good formation, color, and strength, showed little change in color after oven-aging, and compared favorably with those made from new white rags, described herein later.

(3) *Purified wood pulp: D, 100 percent.*—In previous work [4] paper made from purified wood pulp *D* was hard, and therefore not suitable for book paper, but some of the hardness was attributed to the beater roll and beater tackle not being suited to produce from hard long-fibered pulp the desired character of sheet for book paper. It was believed, however, that if the beating could be effected quickly enough to preclude excessive hydrating or gelatinizing of the fibers without

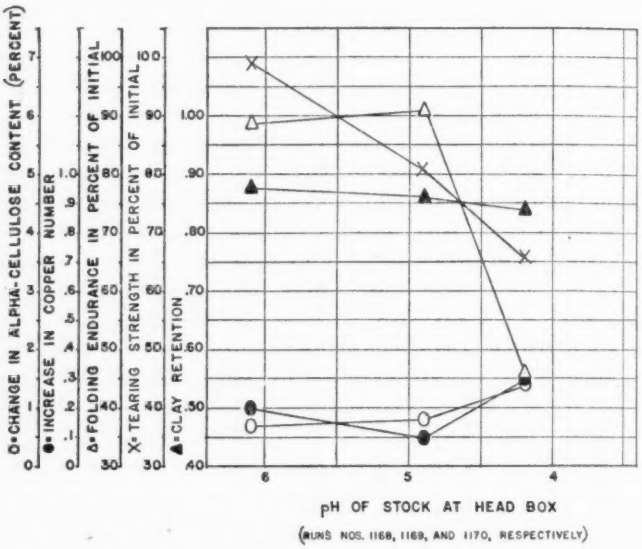

O-CHANGE IN ALPHA-CELLULOSE CONTENT (PERCENT)
●-INCREASE IN COPPER NUMBER
Δ-FOLDING ENDURANCE IN PERCENT OF INITIAL
X-TEARING STRENGTH IN PERCENT OF INITIAL
▲-CLAY RETENTION
pH OF STOCK AT HEAD BOX
(RUNS NOS. 1168, 1169, AND 1170, RESPECTIVELY)

FIGURE 3.—*Effect of acidity on stability of rosin-sized, clay-filled book papers made from purified wood pulp D.*

sacrificing the desired fraying and fibrillation, a soft bulky sheet would result and would have the strength for severe service. Pulp *D* was therefore included in the present study.

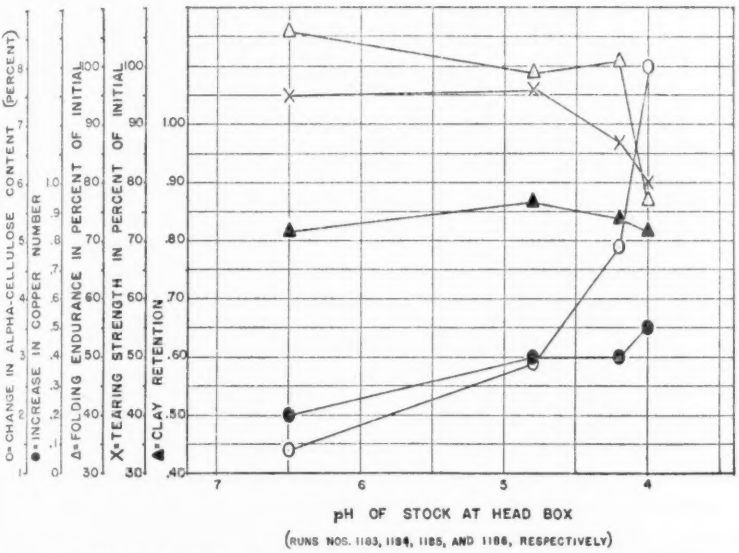
One paper-machine run (1167) was made from the pulp with clay incorporated in the furnish but without rosin size or alum, and a series of runs (1168 to 1170) using 1 percent of rosin size and various amounts of alum. The stability of the sized papers is shown graphically in figure 3.

The papers showed less deterioration in the heat treatment than some of the other pulps, and better clay retention, but the retention decreased as the acidity was increased. Perhaps because of the unfavorable beating conditions, the alum affected the hydrating or binding properties developed in the beater, thereby reducing the slowness of the stock and the amount of filler retained mechanically. As would be expected, the opacity was low and the paper was comparatively hard—more like writing than book.

(4) *Rags: No. 1 new whites, 100 percent.*—Three series of papers were made from new rags and clay filler. One series (runs 1176 to

1178) was without rosin size but with various amounts of alum; the second (runs 1179 to 1182) contained 2 percent of rosin size and various amounts of alum; and the third (runs 1183 to 1186), 1 percent of rosin size and various amounts of alum.

The preparation of the rag half stuff and the method of beating the half stuff to prepare it for the paper machine followed the procedure described in previous publications [3, 4]. When beating the furnish for the rosin-sized papers, however, the stock became very hot as a result of hot weather and hard beating. To preclude any harmful influence of the high temperature on the sizing effect of the rosin, part of the stock was emptied into the chest after the beating was completed so that water could be added to the remainder in the beater before the rosin size was put in. After the rosin size was added, the


O=CHANGE IN ALPHA-CELLULOSE CONTENT (PERCENT)
●=INCREASE IN COPPER NUMBER
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X=TEARING STRENGTH IN PERCENT OF INITIAL
▲=CLAY RETENTION
pH OF STOCK AT HEAD BOX
(RUNS NOS. 1183, 1184, 1185, AND 1186, RESPECTIVELY)

FIGURE 4.—*Effect of acidity on stability of rosin-sized, clay-filled book papers made from new rags.*

stock was circulated about 15 minutes (with the beater roll off the bedplate), the alum was added, and the stock finally mixed in the beater chest.

The folding endurance of the original papers decreased as the alum was increased, the decrease being greatest for the series with the highest rosin content. The unsized papers showed practically no reaction to the heat treatment in retention of folding endurance and tearing strength, and the rosin-sized papers decreased only slightly. An additional run in each of the sized series was made with the amount of alum increased to 4 percent. The resultant papers also were fairly stable. As is apparent from the test data of tables 3 and 4 and the curves of figure 4, if new white rags are properly prepared and the amounts of rosin size and alum added are not excessive, book paper of high stability can be produced.

The papers were not well sized but were satisfactory in this respect for printing. The color, formation, and finish were very good. The retention of clay was maximum when the pH of the stock at the head box was about 5.0. Also, at that acidity the tendency to foam was minimum, not only for the rag stocks but also for the other pulps when rosin size and alum were added.

(5) *Rags: No. 1 old whites, 50 percent; twos and blues, 50 percent.*—The preparation of the rag half stuff from No. 1 old whites and twos and blues also was the same as that used in previous studies [3, 4]. The half stuffs from the two kinds of rags were kept separate until blended in the beater at the time of furnishing. Three series of runs, comparable to the runs described for the preceding pulps in respect of the amounts of clay, rosin, and alum added, were made. One run

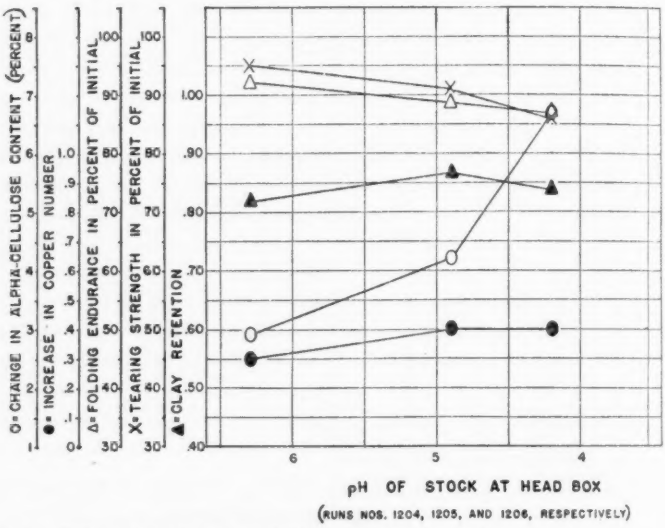
O= CHANGE IN ALPHA-CELLULOSE CONTENT (PERCENT)
● = INCREASE IN COPPER NUMBER
Δ = FOLDING ENDURANCE IN PERCENT OF INITIAL
X = TEARING STRENGTH IN PERCENT OF INITIAL
▲ = CLAY RETENTION
pH OF STOCK AT HEAD BOX
(RUNS NOS. 1204, 1205, AND 1206, RESPECTIVELY)

FIGURE 5.—*Effect of acidity on stability of rosin-sized, clay-filled book papers made from old rags.*

(1214) without clay filler but with rosin size and alum was also included.

The first two runs of old-rag papers (1191 and 1192) without rosin size but with alum showed little change in physical and chemical tests after heat treatment, but the paper of run 1193, with pH 4.2 at the head box, showed a decided decrease in alpha-cellulose content and retention of folding endurance. The clay retention was practically the same for all three runs.

For both series of the rosin-sized papers (2 percent, runs 1200 to 1203; 1 percent, runs 1204 to 1206) the measurements given in table 4 show increases in the change of alpha-cellulose and copper number as the alum was increased, but the initial folding endurance (table 3) of the papers was so low that the decrease for the heat-treated samples was not pronounced. Clay retention seems to be highest for the old-rag papers when the pH value at the head box is approximately 5. Characteristics of the series sized with 1 percent of rosin are shown in figure 5.

(b) TITANIUM-DIOXIDE-PIGMENTED PAPERS

Titanium dioxide pigments are manufactured pigments said to produce a high degree of opacity and brightness in paper. Although the manufacturer reported that only small proportions of titanium dioxide pigments are generally used in paper, since our study was concerned mainly with the effect of the pigments on stability, 5 and 15 percent were each used in the experimental runs. The method of furnishing the beater was the same for the titanium dioxide pigments as for the clay filler.

(1) *Sulfite pulp, 50 percent; soda pulp, 50 percent.*—Two paper-machine runs (1147 and 1145) were made with 15 and 5 percent of titanium dioxide pigment *A*, at pH values 4.8 and 5.0, respectively, at the head box; and two runs (1148 and 1149) with 15 percent of titanium dioxide pigment *B* but with different amounts of alum. The beater furnishes all contained 1 percent of rosin size.

The opacity of the paper for which 5 percent of titanium dioxide pigment *A* was added in the beater was equal to that of the runs in which 15 percent of clay was used; and when 15 percent of titanium dioxide pigment, *A* or *B*, was used the opacity was better. The papers containing titanium dioxide pigments were whiter and brighter than the clay-filled sheets. The relative quality of the clay and of the other fillers should be regarded as applying only to materials that were representative at the time the work was done. The relationship may be changed with further improvement of fillers. The sizing values were not affected by the pigments. The stability of the titanium-dioxide-pigmented papers was about the same as that of the clay-filled papers.

The original folding endurance and tearing strength of the paper in which 5 percent of pigment *A* (run 1145) was used were higher than when 15 percent of clay or titanium dioxide pigment was used. To maintain high strength and at the same time obtain high opacity is a result desired in filled papers. Since strength is adversely affected as the amount of filler is increased, relatively high opacifying power is a very desirable property. The retention of titanium dioxide pigment *B* increased as the amount of alum added was increased.

(2) *Rags: No. 1 old whites, 50 percent; twos and blues, 50 percent.*—Runs comparable to those made from the sulfite-soda pulps were made from old rags also. The stock for one (run 1207) contained 5 percent of titanium dioxide pigment *A* and was at pH 4.9 at the head box; for two runs (1208 and 1209) the furnishes included 15 percent of titanium dioxide pigment *B* and varied amounts of alum. All contained 1 percent of rosin size.

As with the sulfite-soda papers, the opacity of the paper (run 1207) for which 5 percent of titanium dioxide pigment *A* was used was as high as that of the papers in which 15 percent of clay was used, and was higher for the runs containing 15 percent of pigment *B*. The finished titanium-dioxide-pigmented papers also were whiter and brighter. The effect of the titanium dioxide pigments on the stability of the papers, and the degree of retention of the pigments, were about the same as for clay.

(c) ZINC-SULFIDE-PIGMENTED PAPERS

Zinc sulfide pigments are manufactured materials said to have high brightening and opacifying value.

The supplier of the zinc sulfide pigments recommends as a precautionary measure that plants having considerable copper equipment "avoid acid conditions so excessive as to attack this equipment and to form a dilute copper solution, as such a condition can dull down the white pigment to an extent dependent upon the amount of copper in solution and the time available for the reaction." The 50-pound beater used at the Bureau is lined with copper, and the stock pipes and screen plates are brass. Since the program of study included the manufacture at pH 4.2 of some papers with each filler, dulling of the papers pigmented with zinc sulfide was expected.

The method of furnishing the beater was the same as that used with clay and with titanium dioxide pigments. The papers were all sized with 1 percent of rosin.

(1) *Sulfite pulp, 50 percent; soda pulp, 50 percent.*—Paper machine runs 1150 and 1151 were made with 15 and 5 percent of zinc sulfide pigment *A*, at pH 4.9 and 5.0, respectively, at the head box; runs 1152 and 1153, with 15 percent of zinc sulfide pigment *B* and various amounts of alum.

All four papers were darkened somewhat, but this condition may have been due to the copper and brass of the equipment and the degree of acidity of the stock. (The odor of hydrogen sulfide was detected at the higher acidities, lower pH's.) As a result the opacity would naturally be slightly higher because relatively more light would be absorbed than if the papers had been whiter and brighter in color. The opacity for the run using 5 percent of zinc sulfide pigment *A* is as high as that of papers made with 15 percent of clay, and the opacities for the runs with 15 percent of zinc sulfide pigments, *A* or *B*, are higher.

The stability of the zinc-sulfide-pigmented papers was as good as of the papers containing the other fillers. The usual copper number test as a measure of degradation is not applicable to papers containing zinc sulfide because it interferes with the chemical reactions in the test; therefore no values are given in the table. The retention of zinc sulfide pigment *B* increased as the proportion of alum in the furnish was increased.

(2) *Rags: No. 1 old whites, 50 percent; twos and blues, 50 percent.*—Runs comparable to the last three sulfite-soda runs with zinc sulfide pigments were made with old-rag half stuff also. The test data indicate that as to stability the zinc sulfide pigments had no harmful effect on the papers. But the papers were discolored, which could be attributed in part at least to the copper and brass equipment and the degree of acidity.

(d) CALCIUM-CARBONATE-PIGMENTED PAPERS

Two types of calcium carbonate pigments were used in this study, precipitated and water-ground natural material. When the work was begun only two samples were considered, one of each kind, the precipitated and sample *A* of the natural. Later two more samples, *B* and *C*, of the water-ground natural calcium carbonate were added. The producer of the water-ground natural pigments stated that the three samples differed only in fineness: "Sample *A*, average particle size 10 microns, nothing larger than 30 microns; sample *B*, average particle size 7 microns, nothing larger than 20 microns; sample *C*, average particle size 2 microns, nothing larger than 7 microns."

The precipitated calcium carbonate was soft and bulky, was more finely divided and more uniform in particle size, and when mixed with water stayed in suspension for a comparatively long time. The water-ground natural material was not so soft nor so bulky as the precipitated, and settled out of the water mixture more rapidly. The analyses (table 2) of the two kinds of calcium carbonate show them to be about the same chemically, and they were approximately alike in color.

Most book paper in which alkaline fillers are used is not sized, has no acidic material added, and consequently the stock is alkaline during its manufacture into paper. The general manufacturing practice is very much the same as for the usual clay-filled sheet except for the omission of size and alum. In the experimental work at the Bureau some of the calcium carbonate papers were made without sizing materials, but the pulp for some was rosin-sized first and the calcium carbonate was added later. Before calcium carbonate is used for commercial paper manufacture, however, the patent rights on the use of the material in sized papers should be examined.

(1) *Sulfite pulp, 50 percent; soda pulp, 50 percent.*—In preparing the sulfite-soda stock for the papermaking runs the pulp mixture was beaten first, and the subsequent operations depended on whether the stock was to be rosin sized. The procedure followed for each run is described under the discussion of the run.

The precipitated calcium carbonate was used in runs 1158 and 1159 and 1172 and 1173. In run 1158 the calcium carbonate slip was added when the stock was being discharged into the beater chest. No rosin size or alum was added.

The pulp for run 1159 was sized in the beater and the calcium carbonate was added later in the machine chest. Two percent of size was used, based on the weight of pulp and calcium carbonate, or 2.3 percent if based on pulp alone. The sized stock was allowed to stand overnight in the beater chest. The pH of the stock, before the calcium carbonate was added, was 5.0. The calcium carbonate was added 1 hour before the stock was run over the paper machine.

Run 1172 duplicated run 1159 except for the interval between the addition of the rosin size and the calcium carbonate. For run 1172 the rosin size was added to the pulp in the beater 1 hour before it was discharged into the chest and ½ hour before the alum was added. After being emptied into the beater chest the stock was agitated for a short time and then pumped to the machine chest. The pH of the stock in the beater chest was 5.0. The calcium carbonate slip was added in the machine chest and the stock was agitated for 1 hour to insure uniformity of the mixture. The pH of the stock at the head box was 8.0.

Run 1173 was similar to run 1172, except that 30 percent of precipitated calcium carbonate was added.

The water-ground natural calcium carbonate samples *A* and *C* were used with the sulfite and soda pulp mixture. The stock for run 1174 was prepared without rosin size or alum, but 30 percent of calcium carbonate sample *A* was added in the machine chest. The stock was then agitated for 1 hour to insure a uniform mixture for the paper machine.

For run 1175 rosin size was added to the pulp in the beater 1 hour before the stock was emptied into the beater chest and ½ hour before the alum was put in. After being discharged to the beater chest

the stock was agitated for a short time and then pumped to the machine chest. The pH of the stock in the beater chest was 5.0. Fifteen percent of natural calcium carbonate sample *A* was added in the machine chest, after which the stock was agitated for 1 hour and then pumped to the paper machine. The pH of the stock at the head box was 7.7.

Run 1220 differed from run 1175 only in that 30 percent of calcium carbonate sample *C* instead of 15 percent of sample *A* was added.

Natural calcium carbonate sample *A* (runs 1174 and 1175) settled out of the stock somewhat in the riffler, or sand trap, while being run to the paper machine. This condition was not observed when either the precipitated calcium carbonate or the more finely ground natural calcium carbonate sample *C* was used.

The stock containing calcium carbonate, precipitated or natural, but no size nor alum, did not foam on the paper machine. When rosin size and alum had been added in the beater, however, followed by calcium carbonate in the machine chest, there was foaming on the paper machine, more for the precipitated than for the natural samples, although the amount was not great and doubtless could have been kept down satisfactorily with a fine water spray. There is, of course, always the possibility when foaming has occurred of foam spots being left in the finished paper.

The sizing values reported in table 3 for the sized papers are not high, but appraised by personal opinions and judgment the papers were sized sufficiently to be written on with ink and for ordinary printing processes. There is no direct correlation between the resistance of paper to water penetration and its ink-receptiveness. The retention of the calcium carbonate and the opacity of the papers were good.

From the physical and chemical test data it appears that papers containing calcium carbonate are more stable than the usual rosin-sized papers, which are acid in character.

(*2*) *Rags: No. 1 old whites, 50 percent; twos and blues, 50 percent.*— In the runs with old rags the calcium carbonate slip was added to the stock in the machine chest and the resultant mixture was agitated for 1 hour before being pumped to the paper machine.

Precipitated calcium carbonate, 15 and 30 percent, respectively, was used in runs 1215 and 1216.

The three paper-machine runs (1217 to 1219) with water-ground natural calcium carbonate comprised 15 percent of samples *C*, *B*, and *A*, respectively. As previously stated, the only difference in the three samples was the fineness to which they had been ground, *A* being the coarsest and *C* the finest. In run 1219, as in the sulfite-soda runs with sample *A*, some of the carbonate settled out from the stock in the riffler, or sand trap, but samples *B* and *C* (runs 1218 and 1217) seemed to remain in suspension.

There was no foaming of the stock on the paper machine in any of the runs. The finish of the papers containing the carbonates was satisfactory. All the carbonate-filled papers were comparatively stable.

2. PRINTING TESTS

In the early part of the study, printing tests were made at the Government Printing Office on the experimental papers that had

been manufactured up to that time. The papers printed were representative samples of sulfite-soda runs containing clay (unsized and sized sheets), titanium dioxide pigment *A*, zinc sulfide pigment *A*, and calcium carbonate (precipitated and natural); and of purified-wood-fiber and new-rag papers containing clay.

The papers were printed from type on one side and by the offset process on the other. The fillers seemed well anchored to the fiber and did not dust out during printing. The papers caused no trouble in the operations and the printings were considered very satisfactory.

Now that the experimental paper-mill work on the book papers has been completed, extensive printing tests to evaluate the printing quality of papers representative of all the different pulp and filler furnishes is in progress and the results obtained will probably appear in a later publication. Final opinion as to the relative values of the different fillers and of the other different papermaking details should await the results of the printings.

VIII. DISCUSSION AND CONCLUSIONS

It is well known that fillers used in large amounts very appreciably reduce the strength of paper. The strength of the experimental papers decreased with increasing filler content, but was influenced by the amount, not the type, of filler present. Because of their effective opacifying quality, smaller amounts of titanium dioxide and zinc sulfide pigments than of clay were sufficient to obtain requisite opacity for printing processes, and the resulting papers were less reduced in strength. All the papers had sufficient strength to withstand the mechanical stresses to which book papers are ordinarily subjected.

There was no pronounced difference in the relative effect of the nonalkaline fillers on sizing. The degree of sizing was very much greater for the sulfite-soda papers than for the rag papers, and the purified wood-fiber papers were in an intermediate position. The nonalkaline fillers had less effect than calcium carbonate in reducing sizing. Although the sizing values of the carbonate papers were not high the papers were sized sufficiently to be written on with ink and for ordinary printing processes. There was no direct correlation between the resistance of the papers to water penetration and their ink-receptiveness.

When rosin size and alum had been added to the stock in the beater and followed by calcium carbonate in the machine chest, the stock foamed somewhat on the paper machine, although the amount of foam was not great and doubtless could have been kept down satisfactorily with a fine water spray.

Maxium clay retention was obtained in the purified wood and rag papers when the pH at the head box was approximately 5, and decreased as the amount of alum was increased. For the sulfite-soda pulp, retention of all the nonalkaline fillers increased as alum was increased. Retention of the calcium carbonate was satisfactory.

The papers containing titanium dioxide, zinc sulfide, or precipitated calcium carbonate pigments had the highest opacity values in the experimental work, and, by personal judgment, gave the best printing results. Only a few of the papers were submitted to the printing tests however. Further tests of the printability of representative samples

of all the papers are in progress, and rating of their printing qualities will probably be reported in a subsequent publication.

Aside from natural aging the best information on the inherent permanence of paper is based on changes in physical and chemical characteristics during accelerated aging tests. The Bureau believes that oven aging rapidly accelerates the slow deterioration caused by impurities in the paper, and that changes in alpha-cellulose content and copper number and the percentage of the original strength retained indicate the comparative resistance to degradation. The change in the cellulose in the accelerated aging seemed to have been from alpha- to beta-cellulose, with no appreciable difference in the percentage of gamma-cellulose. The rag and purified wood-pulp papers were more stable to the heat test than the sulfite-soda wood-pulp papers. Nonalkaline fillers had no apparent influence on the stability of any of the papers, and the calcium carbonate pigments had a protective or inhibiting effect in the accelerated aging.

Acidity was an important factor in deterioration. Attack on the cellulose was increased as the amount of alum was increased, in either the unsized or the rosin-sized papers. The rag fibers seemed to withstand acidity better than any of the other fibers used. Contrary to the reaction with the pulps of higher initial purity, sulfite-soda papers were more stable to the heat test when containing rosin sizing than when made with corresponding acidity but without size.

The effect on the stability of increasing the amount of alum in the beater and then neutralizing part of the alum with sodium carbonate as the stock was being pumped from the beater chest to the machine chest was practically the same as having had the final pH value originally in the beater and maintained throughout the preparation of the stock.

The necessity for employing only minimum amounts of rosin and alum in the sizing of papers intended to be used for permanent records is generally recognized. The optimum pH value for combining high stability with adequate sizing of papers containing nonalkaline fillers, however, varies in different mills because of hardness of water, white-water recovery, kinds of materials used, etc., but at the Bureau is approximately 5 at the head box of the paper machine. The pH (hot-water extraction) of the finished papers is in approximate agreement with that of the stock at the head box.

Resistance of paper to deterioration from internal causes is not sufficient to insure its stability, however. The conditions under which the paper is stored and used must also be considered. For a discussion of external deteriorative agencies—light, temperature, humidity, acidic pollution of air—and recommendations as to storage conditions for prolonging the life of paper, the reader is referred to a previous Bureau publication [9].

The authors acknowledge their indebtedness to R. W. Carr of this Bureau for the physical testing of the experimental papers, and to H. F. Launer, C. I. Pope, and W. K. Wilson, also members of the Bureau staff, for the chemical testing of the pulps and papers.

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CESIUM DISCHARGE UNDER CONDITIONS OF NEARLY COMPLETE IONIZATION

By Fred L. Mohler

ABSTRACT

Measurements of the spectral-intensity distribution of the continuous recombination spectrum have been used to measure electron concentration, N_e, and electron temperature, T_e. Using radiation from a 1-mm capillary tube viewed end on, it has been possible to extend measurements to a current density of 300 amperes at pressures up to 17 mm. With increasing current the intensity reaches a flat maximum, and this maximum increases as the square of the pressure. Above 0.3-mm pressure T_e is independent of pressure and increases linearly with current. The observations agree quantitatively with the theory that the cesium in the capillary is in temperature equilibrium at a temperature T_e and a pressure equal to the vapor pressure.

Electrical measurements of T_e and N_e have been made in a 5-mm tube with pressures ranging from 0.0045 to 0.3 mm. In this range T_e increases with decreasing pressure. The gas temperature is not in equilibrium with T_e, and N_e has a value which is higher than that corresponding to temperature equilibrium.

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I. INTRODUCTION

In an electric discharge there is commonly what is termed a plasma. The positive ions, because of their low mobility, produce a positive space charge which holds the electrons in the space, and the electric field resulting from the space charge is limited to a thin sheath over the walls of the tube. In the space there is an electron gas mixed with the atomic gas and by means of electrical measurements with probe wires, the energy distribution and concentration of the electrons can be measured. This energy distribution is commonly a Maxwell distribution and is conveniently expressed as a temperature. The definition of electron temperature is based solely on the kinetic theory conception of temperature, with no implication as to the existence of equilibrium between atoms and electrons.

A series of papers [1] on the interactions of electrons and atoms in the cesium discharge has shown that with increasing pressure and current density there is an approach toward equilibrium between the state of excitation and ionization of the gas and the electron temperature. With current densities of the order of an ampere and pressures over 0.005 mm the number of atoms in the first excited state is nearly equal to the equilibrium value for a temperature equal to the electron temperature. With pressures less than 0.3 mm the population of higher excited states and ionized states is always less than the equilibrium value.

Two technical limitations make it impossible to apply the conventional methods with higher pressures and currents. First, the use of probe wires to measure electron concentrations is impossible with high currents and high pressures. Second, the vapor pressure, but not the vapor density, is known in the cesium experiments, and in an intense discharge there is no basis for estimating the gas temperature and concentration of neutral atoms.

Several types of experiments, notably the experiments of Elenbaas [2] with the mercury arc, indicate that at pressures of the order of an atmosphere the gas temperature is equal to the electron temperature. However, recent spectroscopic studies by Barnes and Adams [3] indicate that considerations of spectral intensity, intensity distribution, and heat loss lead to three quite different figures for the temperature. These considerations make it of interest to extend the study of the cesium discharge to higher pressures and currents, and this paper describes experiments with methods designed to avoid, as far as possible, the limitations of more conventional methods.

II. METHODS

It has been shown [4] that measurements of the intensity distribution in the continuous recombination spectrum give a basis for measuring electron temperature and concentration, and the method should entirely avoid the limitations of probe measurements. The uncertainty as to the concentration of atoms can at least be minimized if conditions of nearly complete ionization can be attained, for then the number of neutral atoms per cubic centimeter becomes of trivial importance for most considerations.

The continuous recombination spectrum consists of bands extending from each series limit to higher frequencies and the radiation at a frequency interval, $\nu - \nu_0$, beyond the limit comes from electrons with a kinetic energy corresponding to this frequency difference

$$h(\nu - \nu_0) = \frac{1}{2}mv^2 = E. \tag{1}$$

Thus, the intensity distribution in the band depends on the energy distribution, or temperature of the electrons. For the case of the band beyond the subordinate series limit, 6P of cesium, the relation

[1] F. L. Mohler, *Power input and dissipation in the positive column of a caesium discharge*, BS J. Research **9**, 25 (1932) RP455; *Collisions of the first and second kind in the positive column of a caesium discharge*, BS J. Research **9**, 493 (1932) RP485; *Reversal temperature and population of excited states in the cesium discharge*, J. Research NBS **16**, 227 (1936) RP869; *Electron concentration and spectral-intensity distribution in a cesium discharge*, J. Research NBS **17**, 849 (1936) RP948.

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[4] Mohler, J. Research NBS **17**, 849 (1936) RP948.

between the intensity, J_λ, the electron concentration, N_e, and the electron temperature, T_e, have been determined by experiment.[5] A convenient form of the relation for the present purpose is

$$\lambda_e J_\lambda = 0.516 \times 10^{-18} \frac{N_e^2}{T_e^{3/2}} e^{-E/kT_e}, \tag{2}$$

where J_λ is the radiation flux, in ergs, in all directions in unit range of wave length (λJ is independent of the unit). It follows that a plot of log λJ versus E gives a line of slope inversely proportional to T_e, while the intensity at the limit ($\lambda = 0.5\ \mu$) is [6]

$$J_\lambda = 1.03 \times 10^{-18} N_e^2 / T_e^{3/2}. \tag{3}$$

At pressures less than 0.3 mm it has been possible to use an electrical method of measuring T_e and N_e. The random electron-current density was too high to measure with a positive probe, but it was possible to measure the positive current to a probe flush with the wall, and also the electron current reaching this electrode at potentials a volt or more negative with respect to the space potential. The electron temperature was obtained from these measurements by the usual semilogarithmic current-voltage curves. The electron concentration at the axis of the tube is related to the positive-ion current density by the "ion-current equation".[7]

$$N_e = 2.08 \times 10^{16} I_+ T_e^{-1/2}. \tag{4}$$

This equation has been derived for the case of low pressure and long mean free paths, but experience shows that it remains approximately true at fairly high pressures.

III. PROCEDURE

In order to obtain high current densities without the use of excessive currents, a section of narrow tubing between two wider tubes has been used. Figure 1 illustrates the type of tube used for the spectroscopic measurement of N_e and T_e. A 1-mm capillary 1 cm long was commonly used, and for extreme conditions, the capillary was of quartz with quartz Pyrex seals connecting it to the rest of the tube. The discharge was viewed end-on through a thin, blown Pyrex window. The quartz is badly attacked by the cesium, but the Pyrex window was only slightly discolored with vapor pressures as high as 1 cm. The reaction with quartz quickly uses up all of the cesium at pressures above a few millimeters, and exposures had to be planned in advance and made very quickly. Intensities have been measured by densitometer comparison with exposures to a calibrated strip lamp.

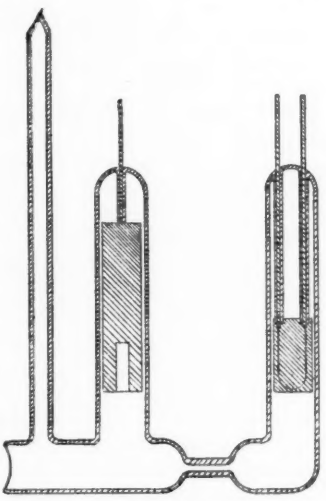

FIGURE 1.—*Type of tube used for spectroscopic measurement of N_e and T_e.*

[5] Mohler, BS J. Research **10**, 771 (1933) RP565.
[6] The 5D continuum overlaps the 6P limit and contributes to the intensity at wave lengths less than 5000 A by an amount which depends on T_e but is of the order of 30 percent.
[7] Tonks and Langmuir, Phys. Rev. **34**, 876 (1929).

There are many factors of uncertainty in this work. There is necessarily a pressure gradient with a high current density,[8] but appearances indicate that this is comparatively small in the absence of foreign gas. Evolution of gas can reduce or extinguish the discharge though the discharge tends to clean up the evolved gas and resume normal operation. The slight discoloration of the glass can be a serious source of error in measuring T_e, and radiation in the line of sight outside the capillary influences the intensity measurements. The time factor has made it impractical to use some obvious precautions to reduce these uncertainties.

Electrical measurements were made in a 5-mm tube with probe surfaces flush with the tube wall. These surfaces were the ends of copper wires 2 mm in diameter, insulated except for the ends with close-fitting glass tubes. The small exposed area and large radiating area prevented thermionic emission from overheating. The 5-mm glass tube could be operated at currents up to 20 amp/cm^2.

At low pressures there is a sharply defined upper limit to the current which can be carried without violent oscillations in current and voltage,[9] though other factors commonly limited the current range in this work.

IV. SPECTROSCOPIC RESULTS

Figure 2 shows a series of 10-sec. exposures at a pressure of 0.3 mm and of 0.1-sec exposures at 4-mm pressure. The striking feature is that there is only a gradual change in intensity with current, with a maximum at intermediate currents, while the change in intensity with pressure is very rapid. The phenomena suggest that single ionization is nearly complete at these currents. At 0.33 mm and 150 amp the spark lines are strongly excited, but probably even in this case the number of doubly charged ions is negligible.

Figure 3 is a plot of spectral-intensity distribution on a scale such that the slope is inversely proportional to the temperature (see eq 2). The results give a definite but not very accurate basis for electron-temperature measurement and show that the temperature increases progressively with increasing current. Ordinates at $E=0$ give the intensity at the series limit, which is a maximum near 75 amp/cm^2 and less than half the maximum value at 150 amp/cm^2.

Figure 4 is a plot of electron temperature as a function of current density and includes measurements at various pressures between 0.3 and 4 mm. Within the range of experimental uncertainty, the points fall on a single straight line. Discoloration of the glass tends to make the measured values low and some series of measurements giving abnormally low temperatures have been discarded.

Figure 5 is a logarithmic plot of intensity near the series limit as a function of pressure. The points are the intensity for a current giving maximum intensity, except for the two highest points which were determined at a single current of 300 amp/cm^2. The slope of the line indicates that the intensity varies nearly as the square of the pressure. The current of maximum intensity increases with the pressure, so a plot of intensity at constant current would give a curve steeper than this at low pressures and of gradually decreasing slope.

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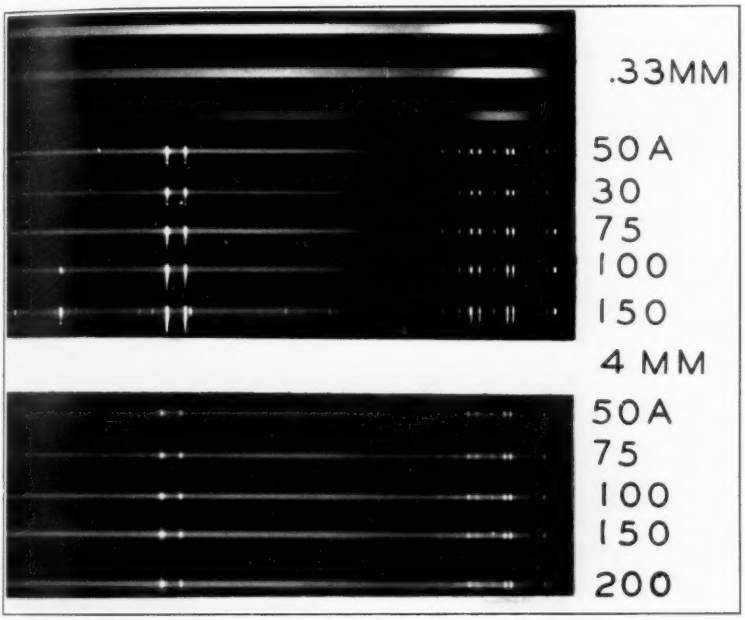

FIGURE 2.—*Spectra of cesium discharge in 1-mm capillary in the range 4000 to 6000 A, left to right.*

The upper group are 10-sec exposures to strip lamp at 1,665° K and to a discharge at 0.33-mm pressure. The lower group are 0.1-sec exposures at 4-mm pressure.

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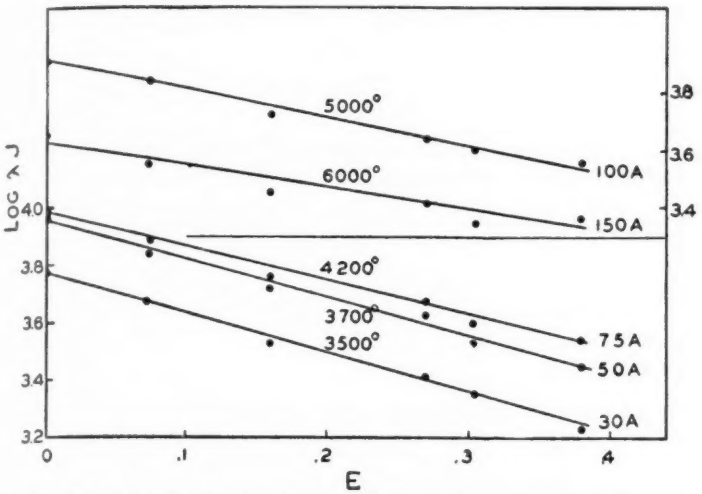

FIGURE 3.—*Intensity distribution in the cesium continuous spectrum between 5000 and 4300 A at a pressure of 0.6 mm, plotted on a scale to give electron temperature, (see eq 2).*

V. INTERPRETATION OF SPECTRA

It is of interest to compare these observations with the intensity of radiation which would be emitted by cesium vapor in thermal equilib-

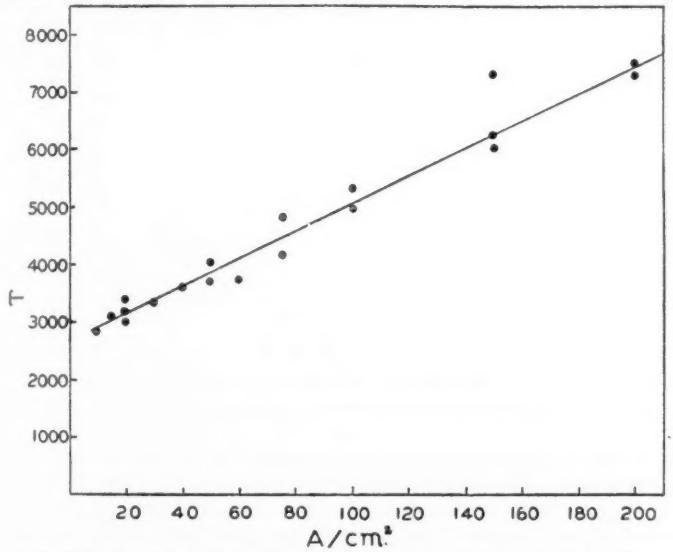

FIGURE 4.—*Electron temperature as a function of current density.*
Vapor pressures between 0.3 and 4 mm.

rium at a given temperature and pressure. The concentration of electrons or ions ($N_e = N_+$) relative to the concentration of normal atoms N_1 is by Saha's equation

$$\frac{N_e^2}{N_1} = 2.43 \times 10^{15} T^{3/2} e^{-E_i/kT}, \tag{5}$$

where E_i is the ionization energy. With the approximation that all neutral atoms are in the normal state

$$N_1 = N_0 - N_e, \tag{6}$$

where N_0 is the concentration of atoms which would exist in the absence of ionization at the given pressure and temperature.

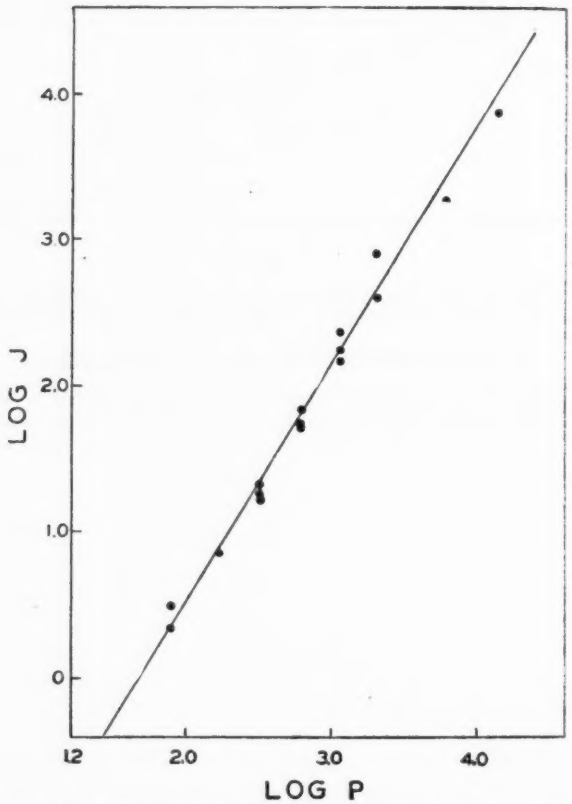

FIGURE 5.—*Plot of intensity as a function of pressure on a logarithmic scale.*
J is intensity at the current of maximum intensity and at 5000 *A*; *P* is pressure in microns.

The value of N_e from eq 5 and 6 substituted in eq 3 gives the intensity radiated by cesium in temperature equilibrium at a temperature T_e. In figure 6 these theoretical values of intensity are expressed as a function of temperature for various pressures. The maximum of each curve is attained when about 90 percent of the atoms are ionized. With a further increase in temperature the decrease in vapor density and in the recombination coefficient more than compensates for the greater percentage of ions. At the highest temperatures plotted the ionization is over 99 percent complete.

In figure 7 the points are observed values of log J as a function of current density at different pressures. The curves are theoretical values of log J for equilibrium at a temperature equal to the electron temperature. That is, they are the curves of figure 6 expressed in

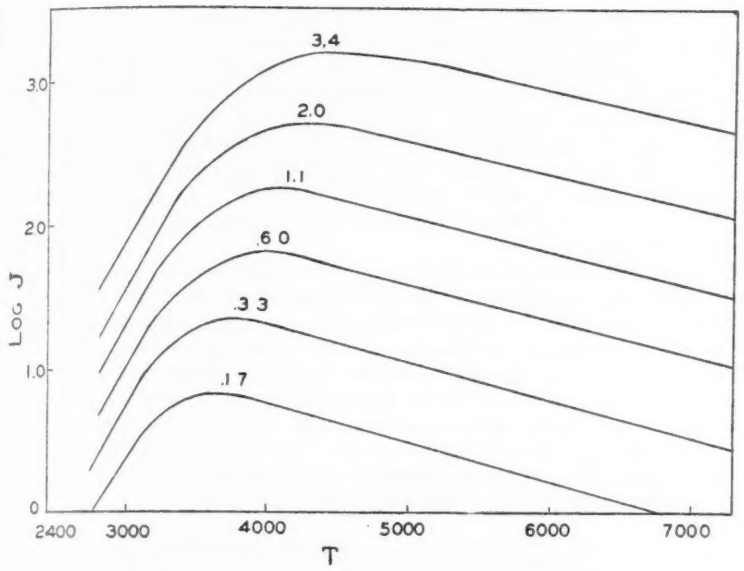

FIGURE 6.—*Theoretical curves of log J as a function of temperature for temperature equilibrium for pressures (mm) indicated on curves.*

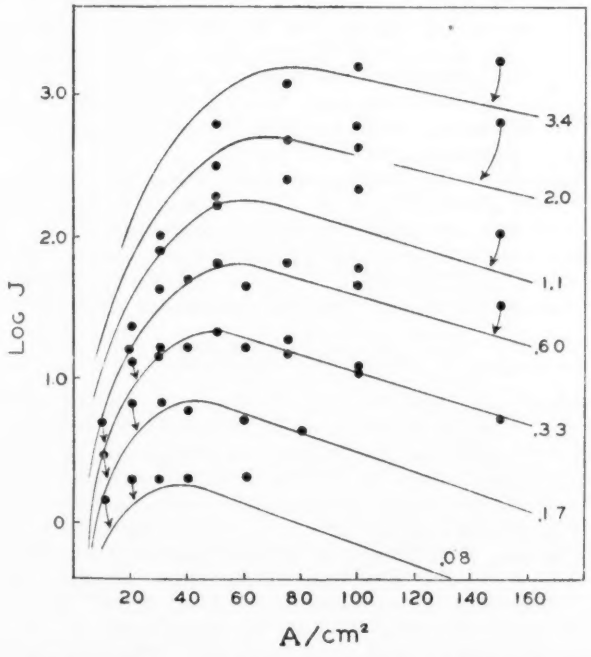

FIGURE 7.—*Points are the measured values of log J as a function of current density, while the curves are theoretical values for temperatures given by figure 4.*

terms of current density instead of temperature by the relation of figure 4. Observations agree with the theoretical curves within the range of experimental uncertainty. At pressures 0.60 and 0.33 mm a correction has been made for radiation outside the capillary; for other cases this was not possible. It is to be emphasized that experimental values agree in absolute value with the theoretical within the limits of error on the assumption that the total pressure in the capillary equals the vapor pressure in the wide tube.[10] At 0.6-mm pressure and 75 amp/cm^2 (4,400° K) the observed value of log J is 5.79 and the computed value 5.88.

It is concluded that for the range of conditions of figure 7 there is approximately equilibrium at a temperature equal to the electron temperature. This is undoubtedly only a rough approximation and more refined methods would give a more complicated picture. Visual observations of the spectrum of the capillary indicate that near the walls the temperature is much lower than at the center for the arc lines are much more intense at the walls, while spark lines and continuous spectrum are stronger at the center. The following results indicate that the gas temperature is not in equilibrium with the electron temperature at pressures much below 0.3 mm.

VI. ELECTRICAL MEASUREMENTS

Electrical measurements in a 5-mm tube have been made in the pressure range 0.0045 mm to 0.3 mm, though the experimental uncertainty is great above 0.08 mm. Electron temperatures, based on semilogarithmic current voltage curves, are shown in figure 8. This figure includes the data from figure 4 for a 1-mm tube, though the temperatures for different tube diameters are not expected to be identical. The figure shows that for low pressures there is a rapid increase in temperature with decreasing pressures in contrast to the phenomena at pressures above 0.3 mm.

Measurements of the electron concentration as a function of current density are given in figure 9. The dots are from electrical measurements based on eq 4 and give the concentration at the axis of the tube. Circles are spectroscopic values for the 1-mm tube based on eq 3 and the data of figure 7. Because of low optical resolution the values pertain to the whole cross section rather than the axis of the tube.

VII. DISCUSSION

The electron concentration as a function of current density has a maximum value at all pressures and this maximum comes at progressively higher currents as the pressure is increased. A comparison of figure 8 and figure 9 shows that this maximum comes at much higher electron temperatures at low pressures than at pressures above 0.3 mm, and this is quite the opposite of what is to be expected with temperature equilibrium. For pressures of 0.039 mm and less the maximum comes at about 8,000° K. The temperature required to maintain 90-percent ionization in equilibrium is about 3,400° K at 0.039 mm and 3,000° at 0.0045 mm. Thus the conditions at low pressures depart greatly from a state of equilibrium. The electron concentration is higher than would exist in equilibrium at the same temperature.

[10] For complete ionization N_e then equals ½ N_0 and not N_0. Curves of figure 6 have not been recomputed but simply changed by a constant factor in figure 7, so they are slightly in error at low currents.

At 0.0045 mm the observed maximum value of N_e is 1.25×10^{13}, while there would be 0.3×10^{13} in equilibrium at 8,000°.

This discrepancy between conditions in a low-pressure discharge as compared with a state of temperature equilibrium at a temperature T_e is entirely in accord with conventional views as to the mechanism of a low-pressure discharge. At low pressures ions recombine on the walls of the tube and evaporate as neutral atoms at a temperature com-

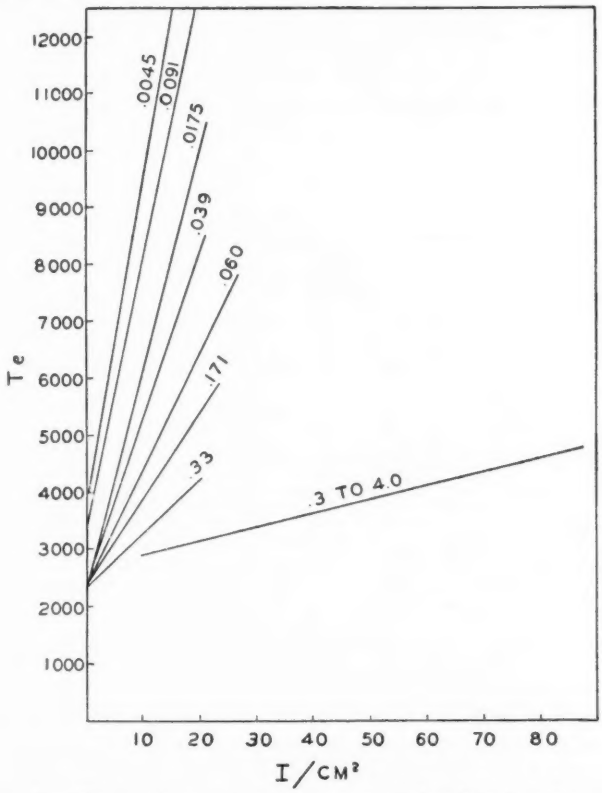

FIGURE 8.—*Electron temperature versus current densities in a 5-mm tube.*

Numbers on the curves are vapor pressures in millimeters. The lower curve gives the data of figure 4 for a 1-mm tube.

parable with the wall temperature. This keeps both the gas temperature and the ion temperature far below the electron temperature, for the momentum given to the ion in ionization by collision is negligible.

The significant new result of this work is that in an intense discharge at pressures as low as 0.3 mm the gas temperature has become nearly equal to T_e. Probably volume recombination has at these pressures become large in comparison with wall recombination and this combined with the short mean free path of electrons in a highly ionized gas makes it possible to maintain a gas temperature far in excess of the wall temperature. The approach to equilibrium between gas temperature and T_e is in the pressure range 0.08 to 0.3 mm. Above 0.3 mm it is safe to assume that the percentage of ionization and the concentration of neutral atoms N_1 are approximately what would be

computed for equilibrium at a temperature T_e. Thus a measurement of any two of the quantities, pressure, N_e, and T_e, determines the conditions in the discharge. At lower pressures there is no basis for estimating N_1 and the percentage ionization.

Theoretical values of the maximum number of ions which can exist in temperature equilibrium at a given pressure furnish a valuable check on experimental methods, and it is very fortunate that with extreme conditions, where experimental errors are greatest, the assumption of temperature equilibrium is best justified. On the assumption that there is temperature equilibrium, the experimental results verify the law of spontaneous recombination, as expressed in eq 2 for electron concentrations ranging from 10^{12} to 10^{16}, correspond-

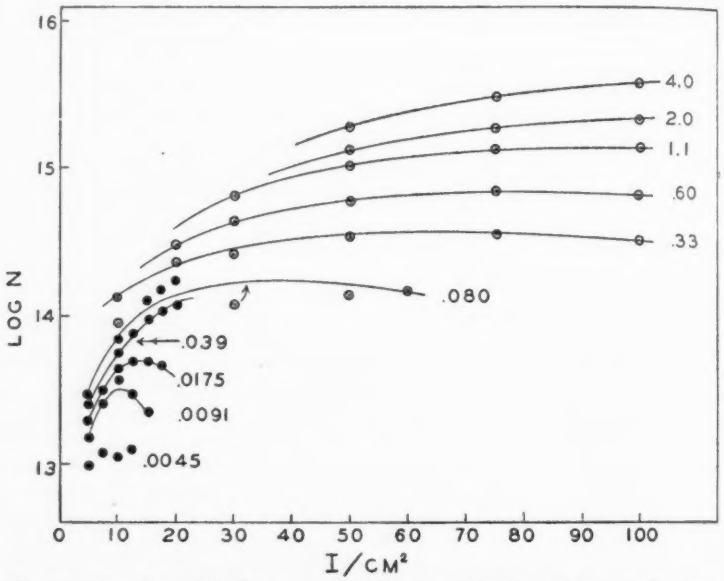

FIGURE 9.—*Log of electron concentration as a function of current density.*

Pressures in millimeters are indicated on each curve. Circles give spectroscopic measurements in a 1-mm tube, and dots are electrical measurements in a 5-mm tube.

ing to a range of 10^8 in intensity.[11] This conclusion is consistent with the postulate of radiation theory that transition probabilities are purely atomic properties independent of pressure, temperature, etc., for the coefficient of eq 2 is a transition probability. A recent paper of Bartels[12] proposes a theory that definitely rejects conventional radiation theory on the grounds that experiments on "Atomgrenz-continua" necessitate such a step. The cesium experiments (the only quantitative experiments) give no support to this viewpoint.

The data presented here on the electron concentration and temperature in discharges of high current density will be used in subsequent papers on the conductivity of an ionized gas and on the number of quantized states that can exist in an ionized gas.

WASHINGTON, August 9, 1938.

[11] This range includes published results with low pressures and currents. J. Research NBS 17, 949 (1936) RP948.
[12] Bartels, Z. Physik 105, 704 (1937).

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